CANMET

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

Metals Technology Laboratories

Laboratoires de la technologie des métaux

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

Canada

THE ENERGY OF OUR RESOURCES • THE POWER OF OUR IDEAS

L'ÉNERGIE DE NOS RESSOURCES • NOTRE FORCE CRÉATRICE

METALS TECHNOLOGY LABORATORIES

HYDROGEN PROBE FIELD PROGRAM - LABORATORY AND FIELD MEASUREMENT OF HYDROGEN IN SOUR GAS PIPELINES

R.W. REVIE, V.S. SASTRI, M. ELBOUJDAINI,
R.R. RAMSINGH AND Y. LAFRENIÈRE

MTL 91-60(TR)

This document is an excerpt
from a report prepared exclusively
for the sole use of the client
organization. It should not be
reproduced without the express consent of
the owners of the Canada Centre
for Mineral and Energy Technology
(CANMET)

Ce document est un rapport
préparé exclusivement pour les clients
de l'organisme. Il ne doit pas être
reproduit sans l'autorisation
écrite des propriétaires du
Centre canadien de
la technologie des minéraux et de
l'énergie (CANMET)

MICROMEDIA

47pp

CANMET

METALS TECHNOLOGY LABORATORIES
REPORT MTL 91-60(TR)

HYDROGEN PROBE FIELD PROGRAM - LABORATORY AND FIELD MEASUREMENT OF HYDROGEN IN SOUR GAS PIPELINES

by

R.W. Revie, V.S. Sastri, M. Elboujdaini, R.R. Ramsingh and Y. Lafrenière

EXECUTIVE SUMMARY

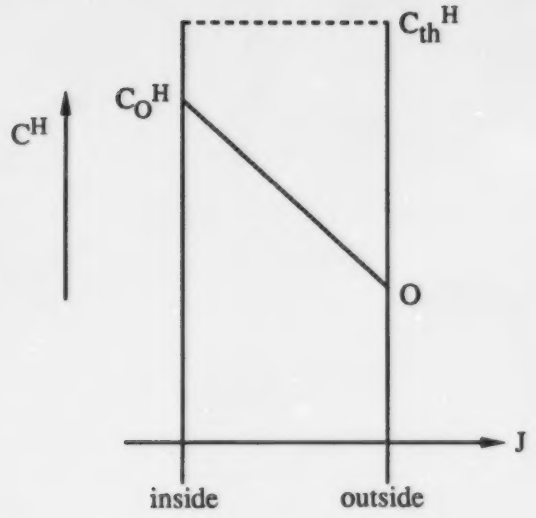
The work described in this report was carried out as part of a project to assess materials for sour service. A pipe containing a sour environment is subject to corrosion on the inside surface, the corrosion reaction being

$$Fe \rightarrow Fe^{2+} + 2e \qquad \text{Eq 1}$$

In parallel to this anodic reaction, the cathodic reaction that must also occur is

$$H^+ + e \rightarrow H \qquad \text{Eq 2}$$

Hydrogen atoms that do not recombine enter the steel surface and diffuse through the steel to the outer surface. Unfortunately, hydrogen sulphide (H_2S) is a poison for the hydrogen recombination reaction so that, in sour media, diffusion of hydrogen through the pipe wall is a process that takes place, with the result that the hydrogen can recombine at so-called "hydrogen traps" in the steel whereby hydrogen-induced cracking (HIC) of the pipe may occur. The type of linepipe steel that is used must, therefore, be resistant to hydrogen-induced cracking. Figure i illustrates schematically the wall of a pipe that is exposed to a sour environment on the inside surface.



C^H - Concentration of hydrogen in the pipe wall

C_O^H Concentration of hydrogen on the inside pipe surface.

J Flux of hydrogen through the pipe wall.

C_{th}^H Threshold hydrogen concentration, above which cracking occurs.

Fig. i. A schematic diagram illustrating a pipe wall exposed to a sour environment on the inside surface.

The objectives of the present work are:

1. To compare test solutions that are used in the laboratory with field environments, by comparing the peak C_O^H values in the laboratory solutions with those in the field;
2. To evaluate a specific line pipe steel for suitability in sour service, by measuring :
   (a) the threshold hydrogen concentration (C_{th}^H) in the steel, above which cracking occurs, and
   (b) the threshold pH (pH_{th}) in H_2S-saturated saline solutions of buffered pH;
3. To compare various means of predicting resistance to cracking in sour service, e.g.,
   (a) by comparing threshold pH, and
   (b) by comparing threshold hydrogen concentration, both diffusible and total hydrogen dissolved in the steel;
4. To assess the effect of inhibitors on reducing the aggressiveness of a sour environment, by assessing the change in peak C_O^H value caused by the addition of inhibitor to a sour environment.

Of the solutions used in the laboratory experiments, the modified NACE TM-02-84 of pH 3.5 solution and the NACE TM-02-84 solution gave the peak C_O^H values that most closely approximated those obtained in the field, with the modified NACE TM-02-84 solution being somewhat more aggressive than the most aggressive field environment, and the TM-02-84 being slightly less aggressive. A summary of the field and laboratory data is presented in the table

below. As indicated, the values of peak C_O^H varied from 5 to 13 μ moles/cm^3 in the lab, depending on the test solution that was used, and the maximum peak C_O^H value in the field was 9 μ moles/cm^3. For this experimental location, the modified NACE TM-02-84 solution would appear to be the best choice of a test environment for evaluating the HIC resistance of steels.

The linepipe steel that was used in these evaluations was highly resistant to HIC. In fact, in the laboratory evaluation of the steel, no cracking could be developed in the steel, even at a pH of 1.1, the lowest pH used. $pH_{th} < 1.1$ and $C_{th}^H > 6.3$ μ moles/cm^3, diffusible hydrogen, 1.5 mL/100 g of steel and 3 mL/100 g of steel of total hydrogen were obtained for this steel.

From the decrease in peak C_O^H caused by the addition of inhibitor, it would appear that inhibition is effective in reducing the severity of a given environment with respect to HIC.

Summary of lab and field data.

Test condition	Medium	D x 10^{-6} cm^2/s	Peak C_O^H (μ moles/cm^3)
Laboratory tests Solution presaturated with H_2S and no inhibitor added	Field produced water	4.8	5.0
	TM-02-84	4.8	8.4
	Modified TM-02-84	4.8	9.9
	TM-01-77	4.8	13
Field tests	Well A	4.8	9
	Well B	4.8	5.6
	Well C*	4.8	3.0

* with added inhibitor

ABSTRACT

Laboratory studies on linepipe steel (AM-2) used in sour service showed:

i. the steel was highly resistant to hydrogen-induced cracking (HIC) even at a pH of 1.1 as evidenced by ultrasonic C-scan patterns;
ii. the pH_{th} of the steel was lower than 1.1, and the threshold hydrogen concentration for cracking was greater than 6.3 μ moles/cm^3; and
iii. the hydrogen concentration at the inside surface of the steel pipe increased with decreasing pH of the medium (5 to 13 μ moles/cm^3 at pH 6.9 to 2.8).

The field studies showed that:

i. the hydrogen concentration inside the pipe surface, peak C_O^H was 9 to 5.6 μ moles/cm^3 at H_2S concentrations of 9.5 and 15.8%, respectively;
ii. the C_O^H value decreased upon addition of inhibitor to the medium;
iii. a laboratory test medium more severe that TM-02-84 appears to more closely reflect the field conditions based on a comparison of peak C_O^H values, with modified TM-02-84 of pH 3.5 as a likely choice.

INTRODUCTION

Linepipe steels used in sour service are prone to hydrogen-induced cracking (HIC), also known as stepwise cracking (SWC), which depends on both metallurgical and environmental factors (1). The metallurgical factors, consist of alloying elements, microstructure, strength, segregation and shape of non-metallic inclusions. Some of the environmental factors causing HIC are the partial pressures of hydrogen sulphide and carbon dioxide, temperature, pH of the medium, moisture and the presence of aggressive ions such as chloride.

Failures of sour gas linepipes have occurred as a result of HIC (2,3). Considerable effort has been expended by steel linepipe producers, users and research organizations to develop an understanding of the mechanism of HIC, to develop a laboratory test method which can identify and quantify material susceptibility to HIC and to produce steels with greater resistance to HIC.

A major concern of linepipe producers and users is how well the laboratory test solutions reflect field conditions. In response to this concern, a three-phase project was developed to:

1. determine which laboratory test solution most closely simulates field conditions based on peak C_O^H values,
2. compare means of ranking material performance in the laboratory, and
3. examine the effect of inhibitors on peak C_O^H values in the field conditions (see Appendix 1a).

Phase I of the lab work was based on the NACE standard HIC test TM-02-84 for evaluating stepwise cracking of linepipe steels (4). The test involves exposing standard coupons cut from the pipe to synthetic seawater solution saturated with hydrogen sulphide for 96 h. The coupons are then sectioned and examined for HIC on planes transverse to the rolling direction. For each crack, the length and extent of stepwise cracking is observed.

Previous work in collaboration with the Canadian Standards Association (CSA) Sour Service Task Force involved the evaluation and comparison of threshold hydrogen concentrations for HIC in nineteen commercial linepipe steels (5). A correlation between the diffusible hydrogen concentration in the coupon and HIC was established along with the existence of threshold hydrogen concentration, C_{th}^H, above which cracking would occur (5). The threshold hydrogen concentrations (C_{th}^H) and threshold pH (pH_{th}) for the nineteen linepipe steels were determined in H_2S-saturated saline buffered solutions. The data on C_{th}^H and pH_{th} of the steels showed that C_{th}^H values greater than 3.5 μ moles/cm^3 (1.0 mL H_2/100 g of steel) indicate good resistance to HIC and that pH_{th} values can be used to rank the steels with respect to HIC resistance (5).

Phase II of the laboratory work was based on the hydrogen permeation method originally developed by Devanathan and Stachurski. Recently, Hay (6) carried out both laboratory and field tests on linepipe steels involving the measurement of the internal surface concentration of hydrogen (C_O^H) and quantification of HIC resistance in terms of crack thickness ratio (CTR) and crack length ratio (CLR).

In a continuation of studies on HIC of linepipe steels, the results are presented in this report for laboratory and field measurements of hydrogen flux in a linepipe steel supplied by the CSA Sour Service Task Force. The objectives were to determine pH_{th} and C_{th}^H for this steel and also the effect of inhibitor on the peak C_O^H value (i.e., the hydrogen concentration at the inside pipe wall), as well as to measure the hydrogen concentrations in the walls of linepipe steel AM-2 operating in the field.

A. LABORATORY STUDIES

PHASE I

Experimental

Sample Preparation and HIC Test Procedure

The ERW linepipe steel [168.3 mm O.D., 7.4 mm wall thickness], designated AM-2, was supplied by the CSA Sour Service Task Force. Table 1 shows the chemical composition and mechanical properties of this material. The long axis of the coupons was oriented parallel to the long axis of the pipe, i.e., in the rolling direction, as illustrated in Fig. 1. Coupons 100 mm long by 20 mm wide by wall thickness were cut from the linepipe sample 180° from the weld. The cut coupons were ground on a wet endless belt and finish ground on dry 600 grit silicon carbide

paper. The specimens were then degreased in acetone. Thereafter, extreme care was taken not to contaminate the coupons, and they were handled with degreased tongs.

Total immersion tests of three coupons cut from parent material 180° from the weld, each weighing ~100 g, were carried out in a buffered solution containing 5 wt % sodium chloride saturated with H_2S at four pH values viz., 1.1, 3.1, 3.7 and 4.3 for 96 h to determine C_{th}^H and pH_{th} values. The test solutions of pH value 1.1 was obtained with 0.1N HCl and that of pH 4.3 with 0.75% sodium acetate plus 0.5% acetic acid. Other pH values were obtained using suitable amounts of potassium hydrogen phthalate and HCl. The specimens were placed in the solution quickly to limit oxygen pickup. A small positive pressure of H_2S in the test cell prevented oxygen contamination from the air. The test duration was 96 h. After testing, the specimens were removed from solution, washed under running water, rinsed in ethanol and dried in a stream of cool air. Each coupon was then placed in a glass cell, and the evolved hydrogen was collected over glycerol at a temperature of 45°C for 72 h, in accordance with a Japanese standard method (7).

Three small samples weighing about 3 g each were also used in total immersion tests and their hydrogen content analyzed by the hot extraction method at 1100°C using the Leybold-Hereaus apparatus.

The glycerol displacement method carried out at 45°C, was used to measure the diffusible hydrogen content; i.e., the hydrogen that diffuses at 45°C, whereas the Leybold-Hereaus method, because of the high temperature used (1100°C) measures the total hydrogen, i.e., diffusible hydrogen plus the hydrogen that is bound or trapped in the metal.

PHASE II

Method 1. Measurement of Hydrogen Flux

Hydrogen flux was measured by a liquid hydrogen monitoring device in a one-sided charging experiment using pipe sections 15 cm (6 in.) long. The pipe section was fitted with polycarbonate covers on the top and bottom. The top cover had openings for a gas inlet and outlet, as well as for the temperature probe and heater (Fig. 2).

Two procedures were followed in measuring hydrogen flux in sour media:

1. In the first procedure, the solution in the pipe was deaerated overnight with nitrogen, and the temperature was maintained at 60°C. At time t = 0, the flow of H_2S was started, and the measurement of the permeation curve began (data given in Appendix 1b).
2. In the second procedure, the solution was deaerated with nitrogen overnight, then it was saturated with H_2S and transferred into the previously deaerated pipe section. Just before the transfer, the solution was heated to 60°C, and this temperature was maintained during the experiment.

The hydrogen flux for the pipeline steel at 60°C containing the following solutions in both the presence and the absence of 250 ppm of inhibitor was measured.

i. NACE TM-02-84, synthetic sea-water (ASTM D1141) without heavy metal ions, pH range 4.8-5.4 after saturating with H_2S.
ii. NACE TM-01-77, 5 wt % NaCl, 0.5 wt % acetic acid, pH of 2.8.
iii. Modified NACE TM-02-84 of pH 3.5 saturated with H_2S.
iv. Field produced water saturated with H_2S.

The design, installation and operation of the hydrogen measuring probe that was used in these studies has been described by Hay (8). The schematic diagram is illustrated in Fig. 3. The external surface of the pipe was prepared according to the following procedure. A 32 mm diameter area of the pipe section where the monitoring device was to be attached was surface finished to 600 grit with the surrounding area masked with epoxy.

Method 2. Determination of Activation Energy, E_a for Diffusion of Hydrogen

A dilute sulphuric acid solution of pH 2.0 containing 10 mg/L As_2O_3 was used in the pipe section. The test set up was similar to Method 1. Data were generated by this method for three temperatures (25, 40 and 60°C) in order to determine the activation energy, E_a for diffusion of hydrogen in the steel. The activation energy was found to be 21 kJ/mole.

Method 3. Determination of the Hydrogen Diffusion Coefficients

It is necessary to determine the value of the hydrogen diffusion coefficient in the pipeline steel so that the hydrogen concentration on the inside wall of the pipe can be calculated. The following method was used to determine the diffusion coefficient:

Electrochemical charging of circular disks of the pipe steel at 25°C was used to generate data which were used to determine the diffusion coefficient. The test solution was identical to that used in Method 2. The experimental set-up used in this method did not permit the determination of diffusion coefficients at temperatures other than room temperature. From the diffusion coefficient determined at 25°C, the value at 60°C was calculated using the activation energy obtained from Method 2 because the temperature in the field is 60°C.

The electrochemical permeation technique used in Method 3 was described by Devanathan and Stachurski (9). Specimens were cut from the pipe wall and machined to 40 mm (1.55 in.) diameter and 1 mm thick. The specimen was ground with SiC grinding paper to 1200 grit. The specimen surface was subsequently polished with γ-Al_2O_3 to 0.3 μm, and rinsed with acetone. Prior to the permeation measurement, the specimen was plated with palladium on the anodic side to eliminate surface effects. The permeation cell consisted of two Pyrex flasks

connected by glass joints with grooves for O-rings. A clamp holds the joints with the sample membrane between them. The exposed specimen area is 6 cm^2. The experimental apparatus is shown in Fig. 4. A 0.1N NaOH solution was used on the anodic side and a 0.1N H_2SO_4 solution (pH 2) containing 10 mg/L As_2O_3 was used on the cathodic side. Both solutions were deoxygenated to reduce background current arising from the reduction of oxygen. By cathodically polarizing the entry side of the sample membrane, hydrogen was produced. On the exit side, the amount of hydrogen diffusing through the membrane was measured as a function of time. The hydrogen was measured electrochemically by maintaining the exit side of the specimen at a constant anodic potential of 250 mV (SCE). At this potential, any hydrogen reaching the exit side is oxidized. In such conditions, the only anodic reaction which can take place is the oxidation of atomic hydrogen, according to the reaction: $H \rightarrow H^+ + e^-$. A potentiostat supplies the current necessary for hydrogen oxidation, and the potentiostatic current is a direct measure of the amount of hydrogen leaving the exit side of the specimen. This current was recorded as a function of time using a computerized data acquisition system.

The data, time and permeation current, were automatically recorded and stored on diskette for further processing. The experiment was terminated when the permeation current had reached a constant level. Diffusion under steady-state conditions is characterized by the type of graph depicted in Fig. 5. The oxidation of hydrogen on the external side results in a permeation curve of the type shown in Fig. 6. After a few hours, a current maximum (I_{max}) is observed, followed by a gradual decrease in I(t) with time until a steady current density is obtained. Mathematical manipulation of the first part of the permeation curve (Fig. 6) yielded values for the effective diffusion coefficient (D) of hydrogen in steel and the hydrogen concentration just below the steel/medium interface (C_O^H), Fig. 5.

Insufficient tests were carried out to enable a statistical analysis of the data.

Detection of Cracks

A Metrotek ultrasonic system equipped with a modified Sperry C-scan recorder operating at 5 MHz was used to detect and locate cracks in the test specimens. Ultrasonic C-scans were obtained on all linepipe test samples before and after exposure to the HIC test media. Both the coupons and the pipe sections were examined in this way for cracking. The coupons were examined over the entire sample size, whereas the pipe sections were examined over the area that was monitored using the liquid hydrogen monitoring device (liquid HMD).

RESULTS AND DISCUSSION

The data on the diffusible hydrogen content of the linepipe steel obtained from total immersion tests at different pH values are presented in Table 2 and Fig. 7. The trend in hydrogen content, going from pH 1.1 to 4.3, obtained by the two methods of analysis, namely the Japanese

glycerol displacement method and the hot extraction method is the same although the absolute values, of course, are different. The hydrogen content of the samples was highest at pH 1.1 and then showed a slight downward trend as the pH increased to 4.3.

Ultrasonic C-scan measurements on the samples before and after total immersion tests at all the pH values 1.1 to 4.3 showed no evidence of cracking even under the most severe test condition – pH 1.1 (Fig. 8 and 9). Thus, it is not possible to define C_{th}^H and pH_{th} values for the linepipe steel, and it appears that this pipeline steel is highly resistant to HIC.

Hydrogen concentration at the inside surface of the linepipe sample was determined by using the hydrogen measuring probe attached to the pipe on the outside, and recording the hydrogen permeation curve as a function of time. Typical curves are shown in Fig. 10. The peak C_O^H values were calculated from the observed maximum of the permeation current using the relationship:

$$\text{peak } C_O^H = \frac{I_{max} L}{DF} \qquad \text{Eq 1}$$

where I is the permeation current density, L is the thickness of the steel pipe (7.4 mm), D is the diffusion coefficient of hydrogen in the steel at the operating temperature and F is the Faraday constant. The diffusion coefficient was calculated by using the relationship:

$$\frac{I_{(t_1)}}{I_{(t_2)}} = \left[\frac{t_2}{t_1}\right]^{0.5} \cdot e^{\frac{-L^2}{4D}\left(\frac{1}{t_1} - \frac{1}{t_2}\right)} \qquad \text{Eq 2}$$

where L is the thickness of the pipe and $I_{(t_1)}$ and $I_{(t_2)}$ are the current densities at times t_1 and t_2, respectively (see Appendix 2).

The experimental data obtained for peak C_O^H values and the diffusion coefficients in the four media studied in both the absence and the presence of an inhibitor are presented in Table 3. The calculated peak C_O^H values increased in going from field produced water through TM-02-84, modified TM-02-84 of pH 3.5, to TM-01-77 paralleling the decrease in pH. The peak C_O^H values obtained in the presence of inhibitor also showed the same trend and were lower than the peak C_O^H values obtained in the absence of inhibitor. The peak C_O^H value determined for the linepipe steel samples containing field produced water medium (Table 3 and Fig. 7) was 5 μ moles/cm^3 which is probably much less than the threshold concentration (C_{th}^H) that could not be obtained in all-side charging tests.

Typical C-scans are shown in Fig. 11(a,b) for a pipe sample before and after exposure to TM-01-77 solution saturated with H_2S which is the most aggressive standard laboratory test environment used. The C-scan patterns were nearly identical, and no cracking was detectable.

CONCLUSIONS

Total immersion tests of linepipe steel AM-2 at pH values 1.1 to 4.3 showed no HIC as evidenced by ultrasonic C-scan patterns. Hence, pH_{th} and C_{th}^H values could not be defined for this linepipe steel, but $pH_{th} < 1.1$ and $C_{th}^H > 6.3$ μ moles/cm^3. The experimental data showed the linepipe steel to be highly resistant to HIC even at a pH as low as 1.1.

The hydrogen concentration at the inside surface of the linepipe samples, peak C_O^H, increased with decreasing pH in both the presence and the absence of the inhibitor. The inhibitor reduced the hydrogen concentration, peak C_O^H.

B. FIELD STUDIES

PHASE III

Experimental

The schematic diagram of the pipeline and the flow of liquid through the pipeline is given in Fig. 13(a). The pipe sections used had the chemical composition given in Table 1, i.e., the same steel that was used in the laboratory experiments. The external surface of the pipe was prepared in the same way as in the laboratory experiments using pipe samples, following the procedure described by Hay (8). The liquid hydrogen measuring device was installed at the 3 o'clock position.

Solid-state hydrogen measuring devices, developed by Morris et al., (14) identified as CH 4, Pt 181 and Pt 180 were attached to the outer surface of the pipe at the 3 o'clock, 6 o'clock and 12 o'clock positions, respectively. Calibration curves for the solid-state probes are presented in Appendix 3. The experimental arrangement of the probes is illustrated in Fig. 13(b).

All the data obtained have no statistical significance since no duplication of the tests was done.

Results and Discussion

Typical permeation curves obtained by using the liquid hydrogen monitoring device are presented in Fig. 14. The upper permeation curve refers to well A containing 9.5% H_2S without any inhibitor. The lower curve refers to well C containing 17.6% H_2S and 250 ppm of commercial inhibitor. The effect of inhibitor is quite obvious in giving a reduced value for C_O^H concentration, notwithstanding the higher concentration of H_2S. The peak C_O^H values were 3 and 9 μ moles/cm^2 with and without inhibitor, respectively.

The permeation curves shown in Fig. 15(a) and (b) were obtained on wells B (containing 15.8% H_2S, no inhibitor) and C (17.6% H_2S plus inhibitor), respectively, at the 6 o'clock position using the solid-state device Pt 181. The values obtained for ΔE for wells B and C were 375 mV and 180 mV, respectively.

The permeation curve for well B using the liquid hydrogen monitoring device did not give a meaningful peak maximum. The permeation curve for well C using liquid HMD gave a value of 13.5 mV for ΔE. Using ΔE values obtained with solid HMD of 375 and 180 mV for wells B and C, respectively, ΔE value of 26.13 mV was calculated for well B, which translates into 5.6 μ moles/cm^3 of hydrogen for this well.

The data for well B shown in Fig. 15(b) were obtained using the solid HMD at the 6 o'clock position. At 3 o'clock and 12 o'clock positions, measurements could not be obtained, possibly because of the absence of aqueous phase at these positions due to the low flow rate of water in this well.

Comparison of Laboratory and Field Data

Comparison of peak C_O^H values obtained in the laboratory tests with field data shows 10 μ moles/cm^3 measured in modified TM-02-84 is in close agreement with 9 μ moles/cm^3 measured in well A. This seems to suggest that a laboratory test medium more severe than TM-02-84 possibly modified TM-02-84 of pH 3.5 more closely reflects the field conditions. With added inhibitor, the measured peak C_O^H value is 3 μ moles/cm^3 in both the laboratory and field tests.

CONCLUSIONS

The field data have shown that:

(i) The hydrogen concentration inside the pipe surface, peak C_O^H values are 9 and 5.6 μ moles/cm^3 in wells A and B containing 9.5 and 15.8% H_2S, respectively.

(ii) The peak C_O^H value in well C containing 17.56% H_2S and inhibitor was 3 μ moles/cm^3 which shows the inhibitor to be effective in reducing the hydrogen concentration.

(iii) For the field where the experiments were done, the modified NACE TM-02-84 solution would appear to be the best choice of a test environment for evaluating HIC resistance of steels.

RECOMMENDATIONS FOR FUTURE WORK

It could be very useful to select a number of operating pipelines where the steels that have been studied (or similar steels) are in use, measure the hydrogen concentrations at the inside surface of the pipe, and compare these values with the threshold hydrogen concentrations determined in the laboratory.

ACKNOWLEDGEMENTS

Numerous helpful discussions with the CSA Sour Service Task Force are gratefully acknowledged, particularly with Malcolm Hay and Kevin Goerz (Shell Canada), Dan Lebsack (Amoco Canada) Pamela Jones (Dofasco) and Michael Enwright (Husky), along with the partial funding of the project by the CPA through the CSA Sour Service Task Force. The assistance of D. Mak and J. Ferry both of CANMET, with the ultrasonic C-scan is also acknowledged.

REFERENCES

1. Biefer, G.J. Materials Performance 21:6:19; 1982.

2. Ikeda, A., Kaneke, T., Hashimoto, I., Takeyama, M., Sumitomo, Y. and Yamura, T. Proc. of Symp. on Effect of Hydrogen Sulphide on Steel; 22nd Annual Conf. Metallurgists; Canadian Institute of Mining and Metallury Edmonton, Canada; 1-17; August 22-24, 1983.

3. Bruckhoff, W. NACE Corrosion '85 paper No. 389; Boston, USA; March 1985.

4. NACE Standard TM-02-84; Test Method - Evaluation of pipeline steels for resistance to stepwise cracking; National Association of Corrosion Engineers; Houston, USA; 1984; Materials Performance 23:5:9; 1984.

5. Hoey, G.R., Revie, R.W., Ramsingh, R.R., Mak, D.K. and Shehata, M.T. Report MTL 88-41(TR); CANMET, Energy, Mines and Resources Canada; Ottawa, Canada; 1988.

6. Hay, M.G. Paper No. 88-39-115; 39th Annual Meeting of the Petroleum Society of CIM; Calgary, Canada; June 12-16, 1988.

7. Japanese Standards Association, Meathod for measurement of hydrogen evolved from deposited metal; Japanese Industrial Standard JIS Z 3113-1975; Tokyo, Japan.

8. Hay, M.G. "An electrochemical device for monitoring hydrogen diffusing through steel"; CIM Conference of Metallurgists; Hydrogen Sulphide Symposium; Edmonton, Canada; 1983.

9. Devanathan, M.A. and Stachurski, Z., Proc. Roy. Soc., A270:90; 1962.

10. Nakai, Y. et al., Corrosion /82, Paper No. 132, NACE, Houston, TX; 1982.

11. Nakai, Y. et al., Corrosion /82, Paper No. 133, NACE, Houston, TX; 1982.

12. Heubaum, F.H. and Berkowitz, B.J., Scripta Metallurgica 16:659-662; 1982.

13. McBreen, J. et al., Electrochem Soc. 113:11:1218; 1966.

14. Morris, D.R. et al., Ironmaking and Steelmaking 16:6:429-434; 1989.

Table 1(a). Chemical composition (wt %) of AM-2*.

C	Si	Mn	P	S	Al	Cr	Ni	Cu	Nb	Ti	N	Mo	Ca
0.08	0.41	0.8	<0.03	0.0016	0.13	0.027	0.015	0.011	0.023	0.019	0.0058	<0.01	0.004

* Determined at the CANMET Chemical Laboratory.

Table 1(b). Mechanical properties of AM-2*.

Yield strength		UTS		Elongation	Hardness
ksi	MPa	ksi	MPa	(%)	(Vickers) 500 g
80	552	84	579	23.6	173 ± 10

* Data provided by the supplier, except for hardness which was measured at CANMET.

Table 2. Diffusible hydrogen in AM-2.

pH of immersion solution	Weight of steel coupon (g)	Glycerol method (45°C for 72 h)			Hot extraction method* (mL (STP)/100 g)
		Diffusible hydrogen content (mL/100 g, 25°C)	STP (mL/100 g)	μ moles/cm^3	
4.3	102.98 101.88 101.64	1.3 1.9 1.8 1.6**	1.5	5.2	2.7
3.7	100.16 98.93 102.08	1.3 1.8 1.7 1.6**	1.5	5.0	2.7
3.1	100.48 101.63 101.72	1.1 1.3 2.2 1.5**	1.4	4.8	3.0
1.1	100.78 101.44 102.65	2.2 1.9 2.0 2.0**	1.8	6.3	3.3

* Leybold-Hereaus

**Average value

Table 3(a). Laboratory data on hydrogen concentration in AM-2 steel at 60°C. Test condition - solution presaturated with H_2S and no inhibitor added.

Medium	pH	$I_{maxL/F} \times 10^{-5}$	D x 10^{-6} cm^2/s	Peak C_O^H μ moles/cm^3
Field-produced water	6.9	2.4	4.8	5.0
TM-02-84	5.4	4.03	4.8	8.4
Modified TM-02-84	3.5	4.8	4.8	10.0
TM-01-77	2.8	6.24	4.8	13

Table 3(b). Field test data for hydrogen in AM-2 steel.

Well	H_2S %	$I_{maxL/F} \times 10^{-5}$	D x 10^{-6} cm^2/s	Peak C_O^H μ moles/cm^3
A	9.5	4.32	4.8	9.0
B	15.8	2.7	4.8	5.6**
C*	17.6	1.44	4.8	3.0

* with added inhibitor

** This value was extrapolated, based on signals obtained with the solid-state hydrogen monitoring device, as explained on page 8.

Table 4. Field conditions.

Well number	H_2S (%)	Water (m^3/D)	Condensate (m^3/D)
A = 10-16	9.5	48	14.4
B = 12-31	15.8	0.4	59.7
C = 12-09	17.6	98.7	10.5

GLOSSARY OF TERMS

pH_{th} - threshold pH value below which cracking occurs

C_{th}^{H} - threshold hydrogen concentration above which cracking occurs

peak C_{O}^{H} - concentration of hydrogen at the inside pipe surface

HMD - hydrogen monitoring device

I - current density

L - pipe thickness

D - diffusion coefficient of hydrogen in the steel

F - Faraday

J - flux of hydrogen through the pipe wall

t - time (s)

ΔE - difference in potential, mV

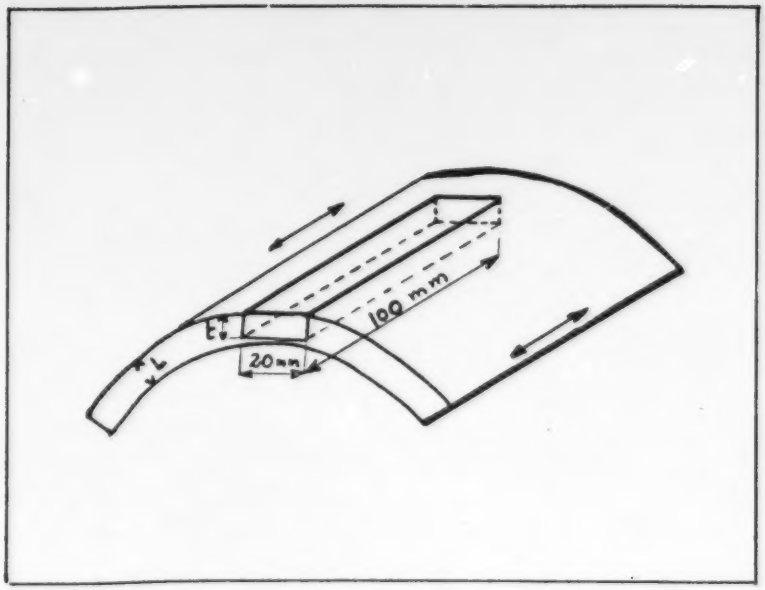


Fig. 1. Orientation of test coupon cut longitudinally from pipeline steel AM-2.

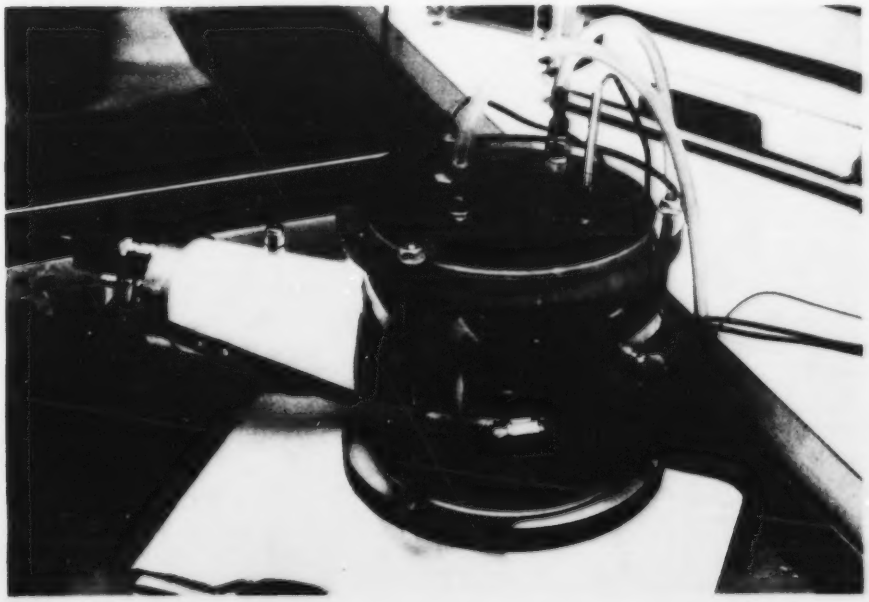


Fig. 2. HIC test apparatus. (neg 20296)

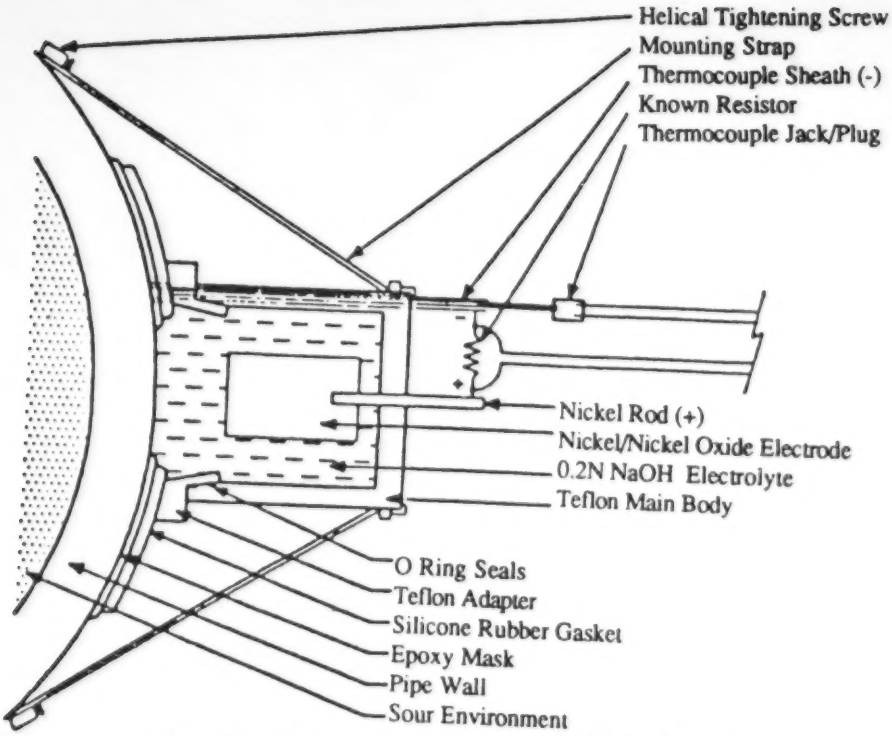


Fig. 3. Schematic of hydrogen monitoring device.

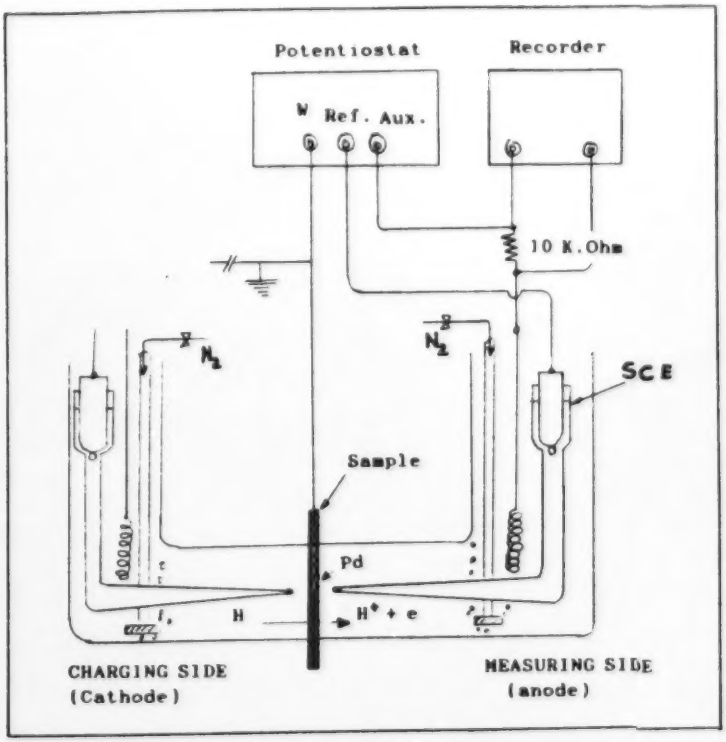


Fig. 4. Schematic of hydrogen permeation cell.

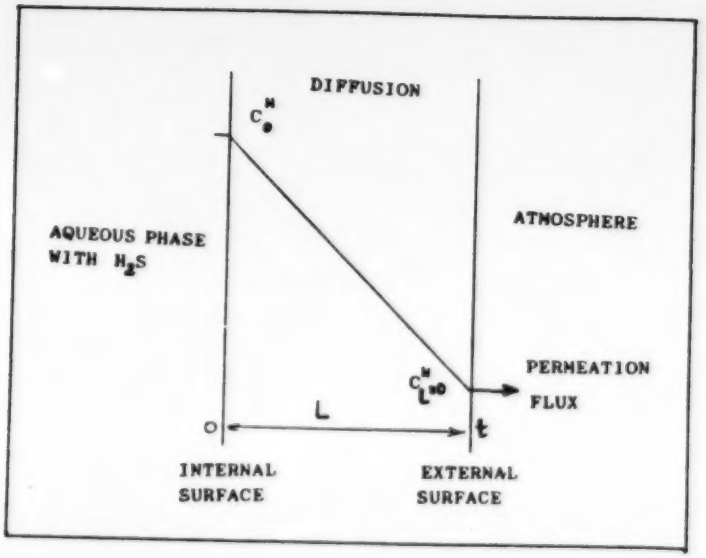


Fig. 5. Hydrogen distribution in the pipe wall.

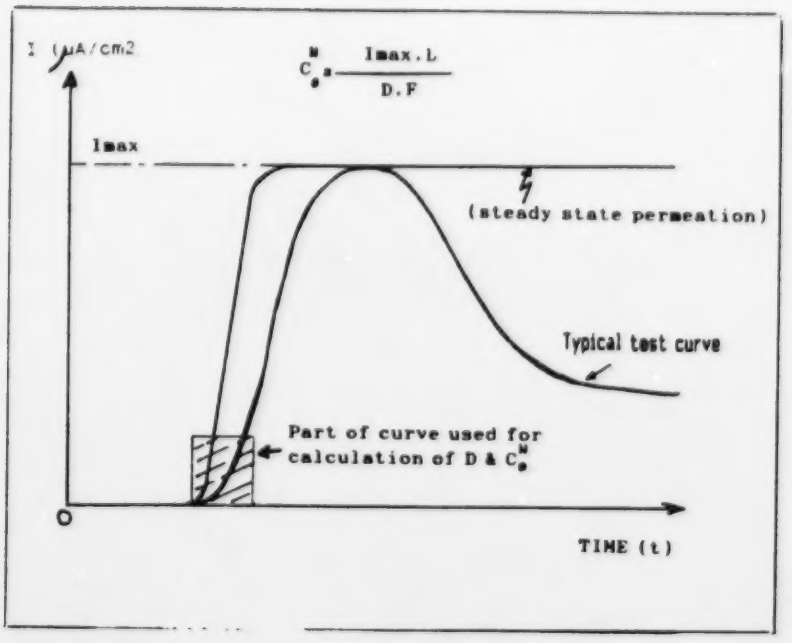


Fig.6. Hydrogen permeation curve.

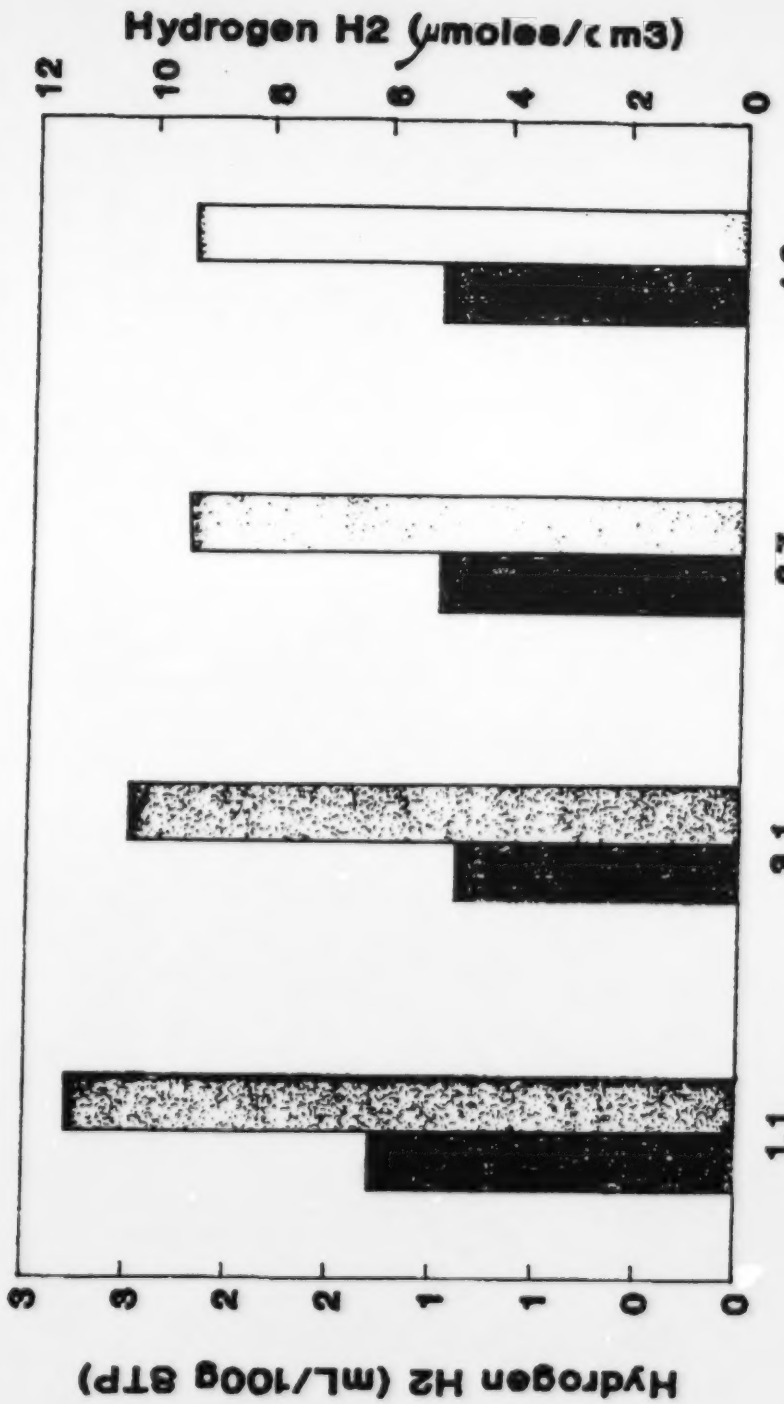
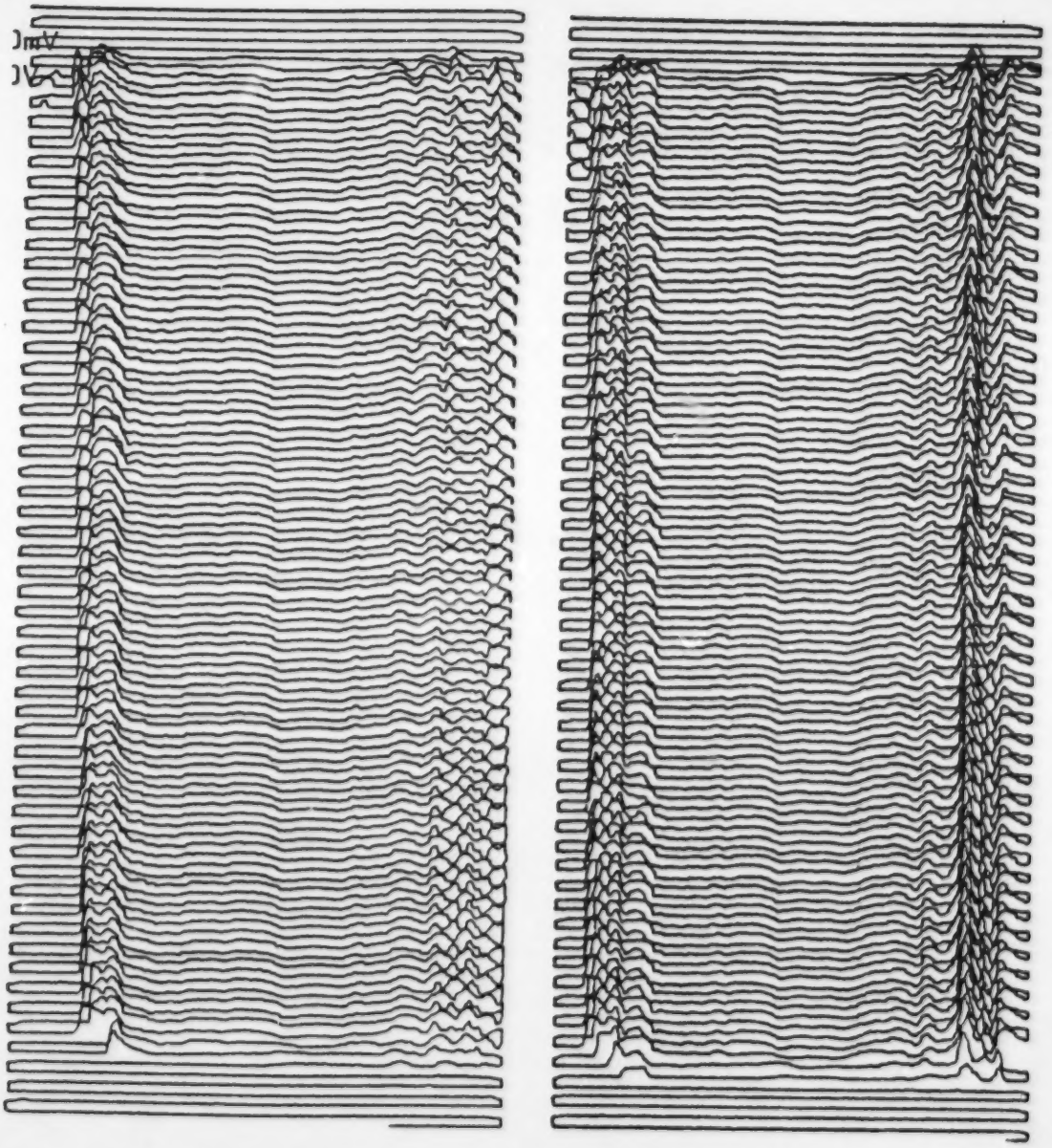


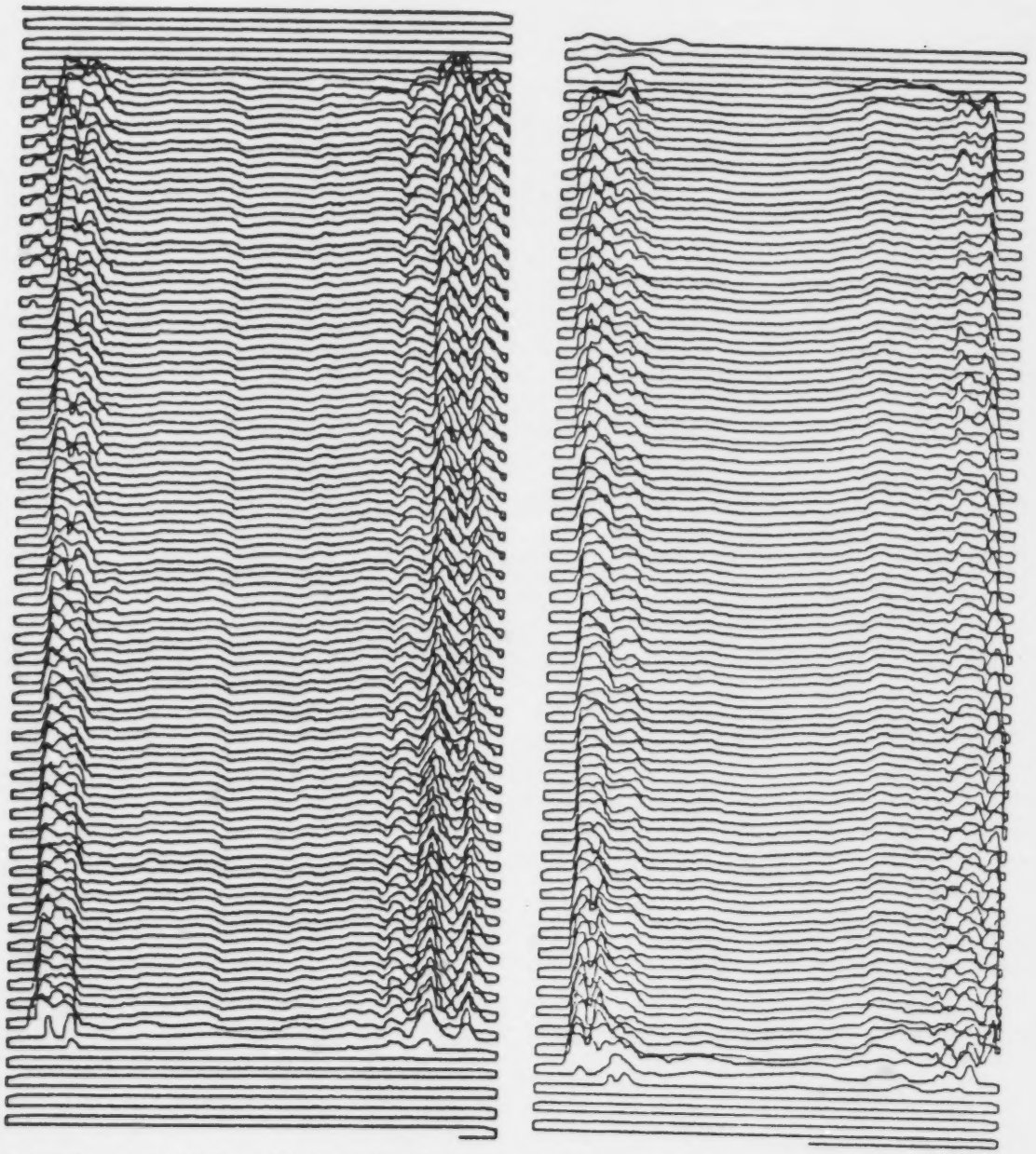
Figure 7: Hydrogen content of AM-2 steel (mL/100g), μmoles/cm3 using diffusible hydrogen (glycerol 45C, 72 h) technique and total hydrogen (hot extraction, 1100C) technique.



(a) C-Scan of AM-2 steel before charging.

(b) C-Scan of AM-2 steel after charging at pH 4.3.

Fig. 8.



(a) C-Scan of AM-2 steel before charging.

(b) C-Scan of AM-2 steel after charging at pH 1.1.

Fig. 9.

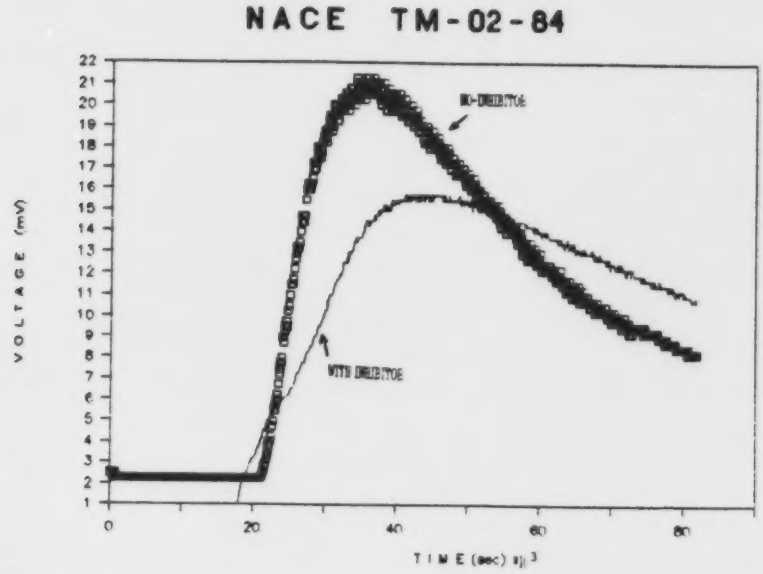


Fig. 10. Hydrogen permeation curves of AM-2 steel in TM-02-84 medium, with and without inhibitor.

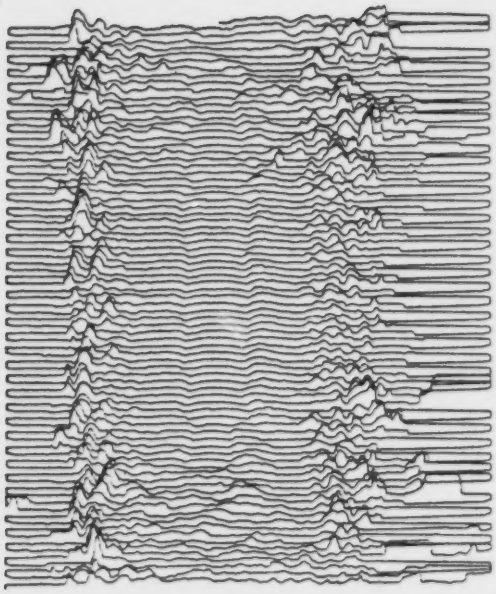


Fig. 11 (a) C-Scan of AM-2 steel before test.

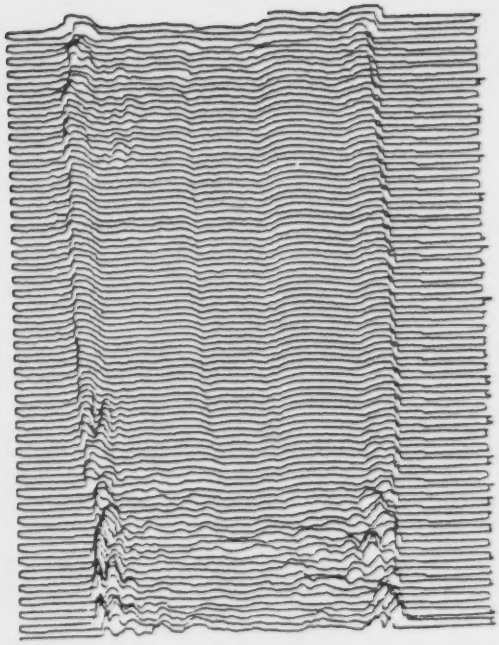


Fig. 11 (b) C-Scan of AM-2 steel after test in TM-01-77.

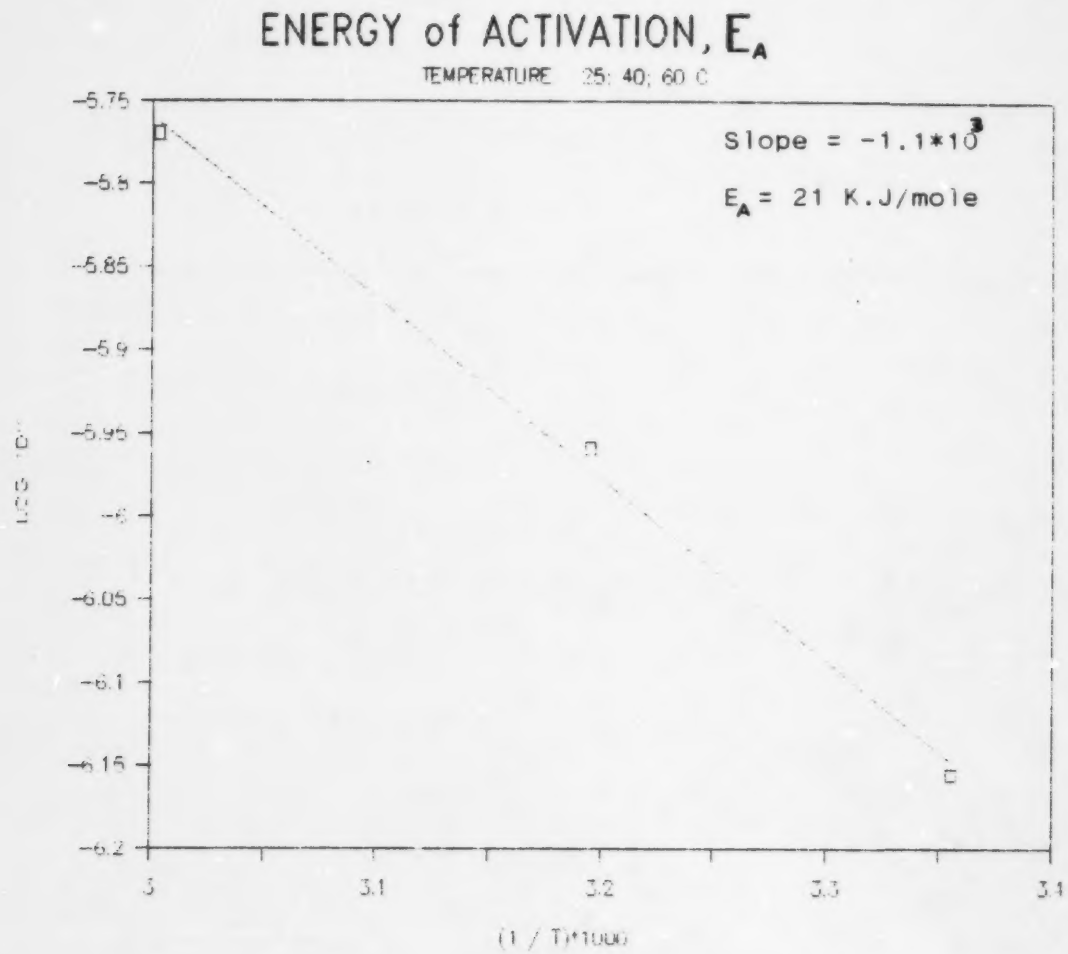
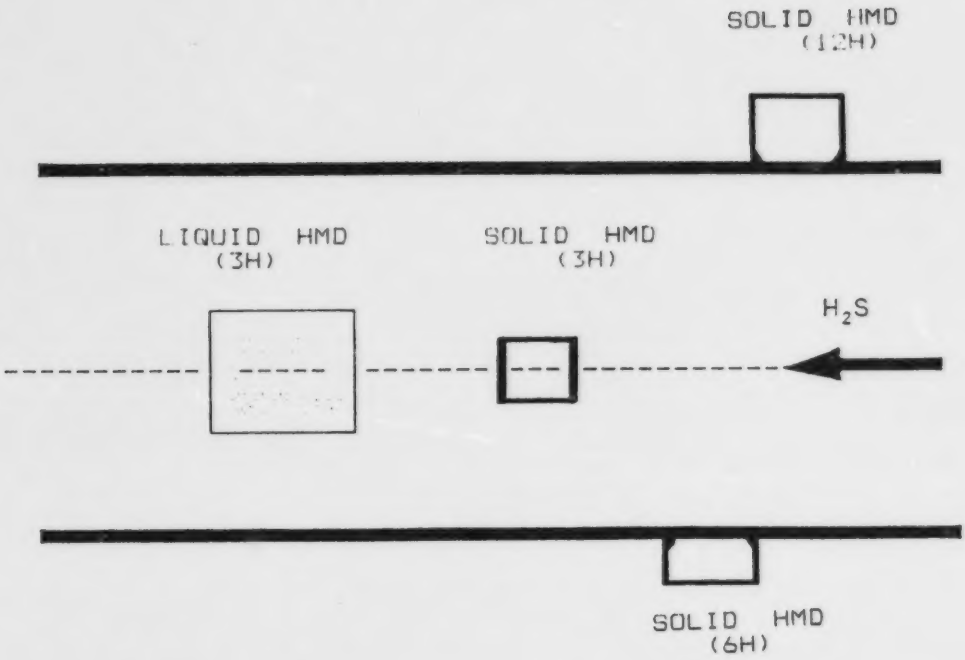


Fig. 12. Variation of diffusion coefficient D , with temperature 1/T.



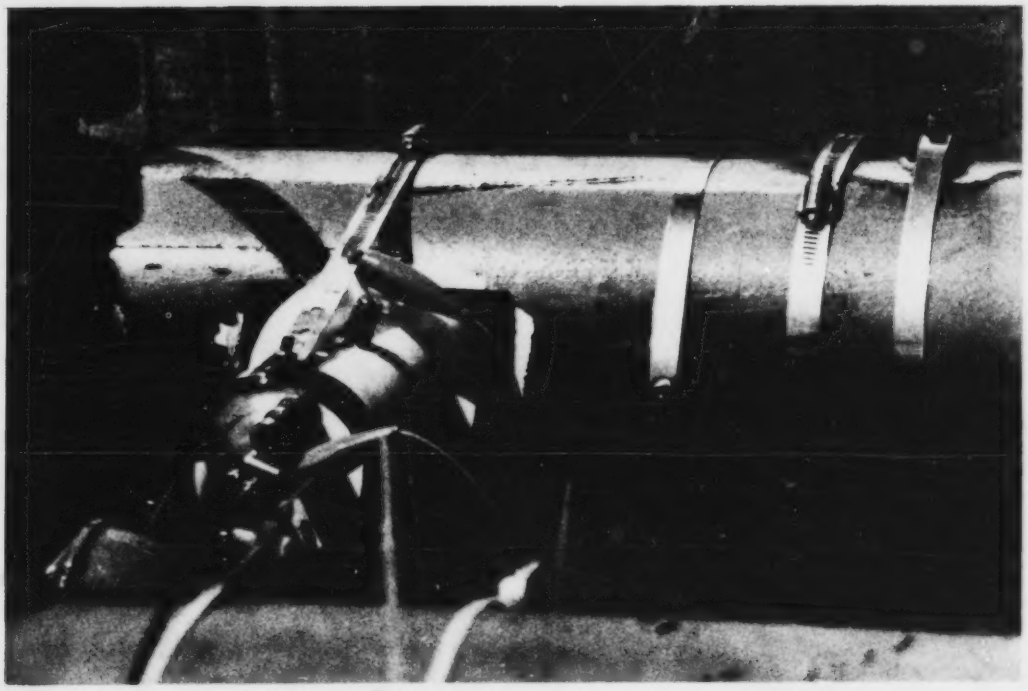


FIG. 13 (a,b) Hydrogen probe arrangement in field tests. (neg 20279)

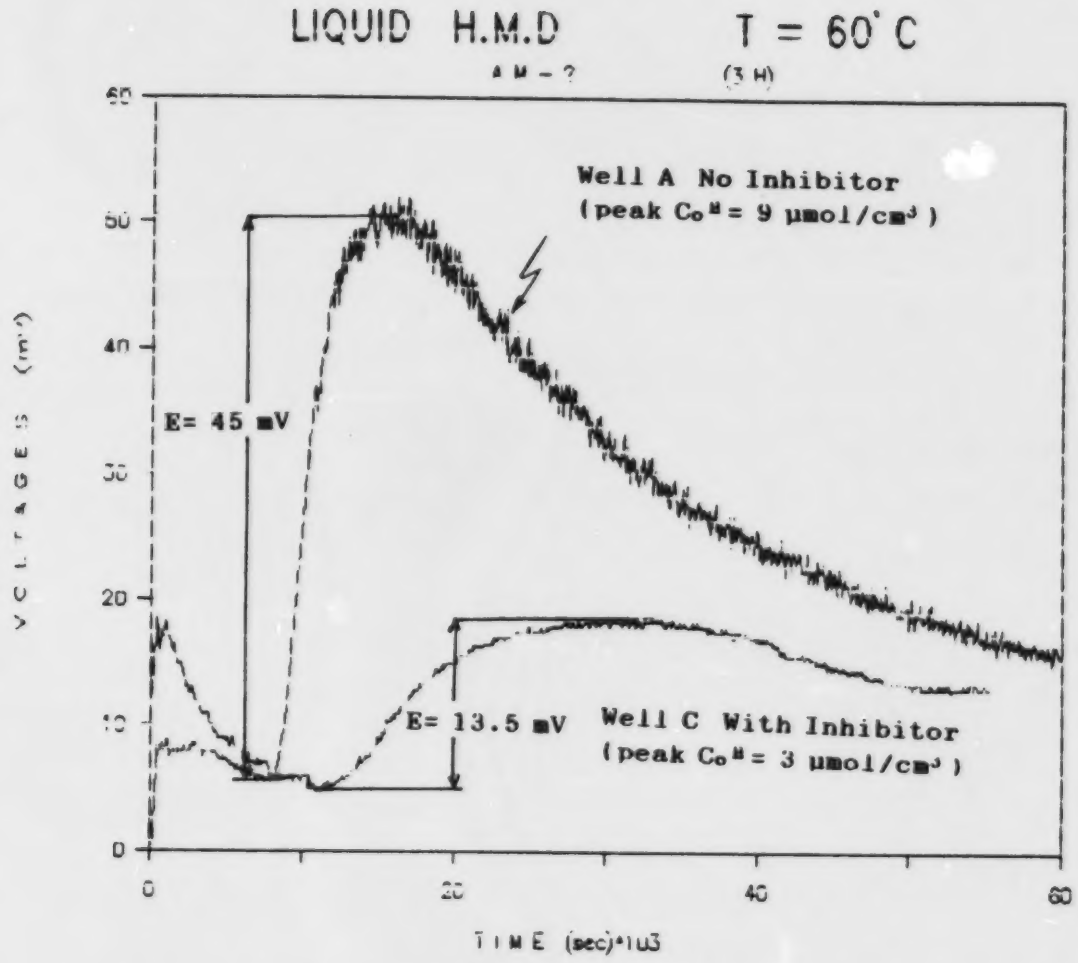
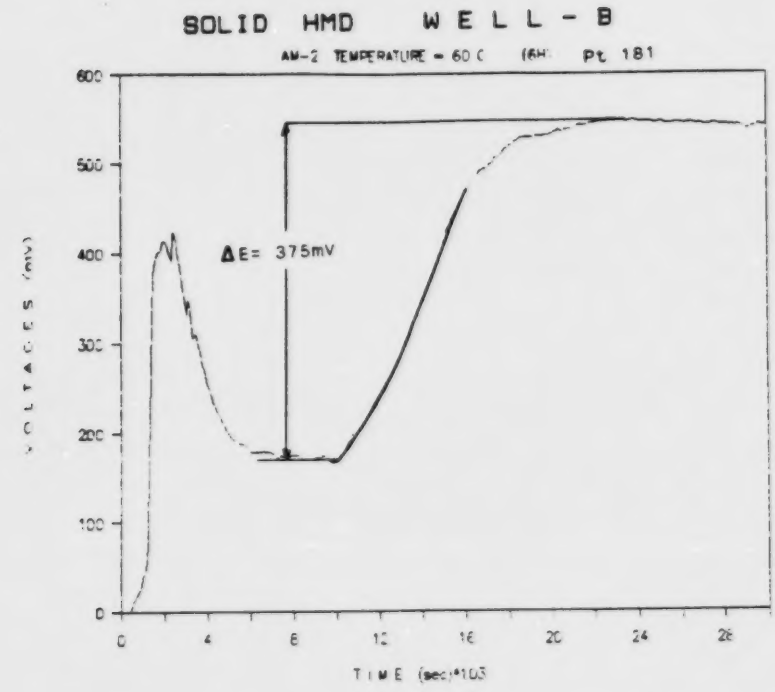
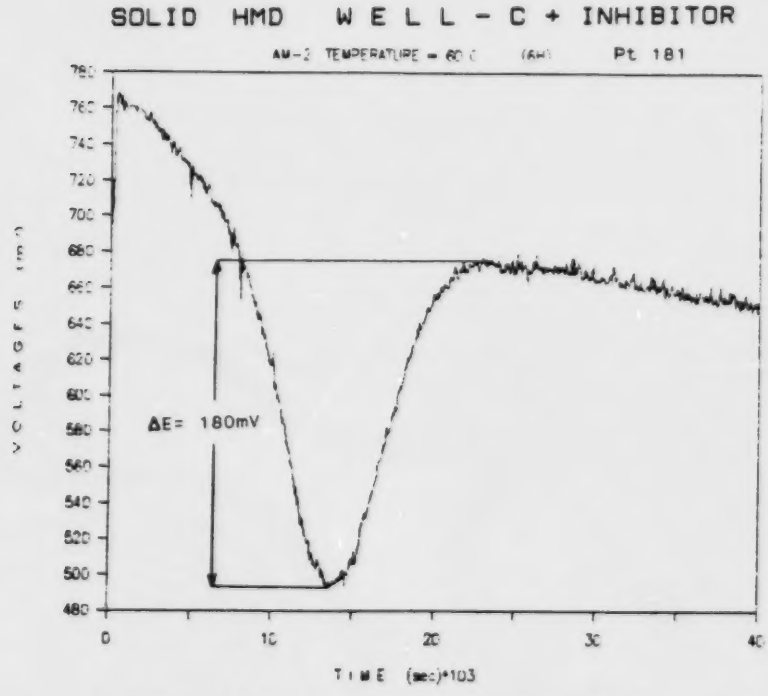


Fig.14- Hydrogen permeation curves from field tests for wells A and C.



(a) on well **B** containing 15.8% H_2S no inhibitor added



(b) on well C containing 17.6% H_2S with 250 ppm of inhibitor added.

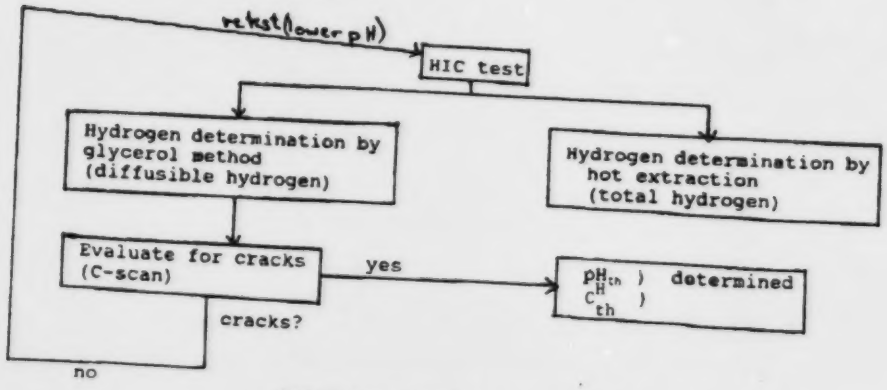
Fig. 15- Hydrogen permeation curves obtained with solid state HMD.

APPENDICES

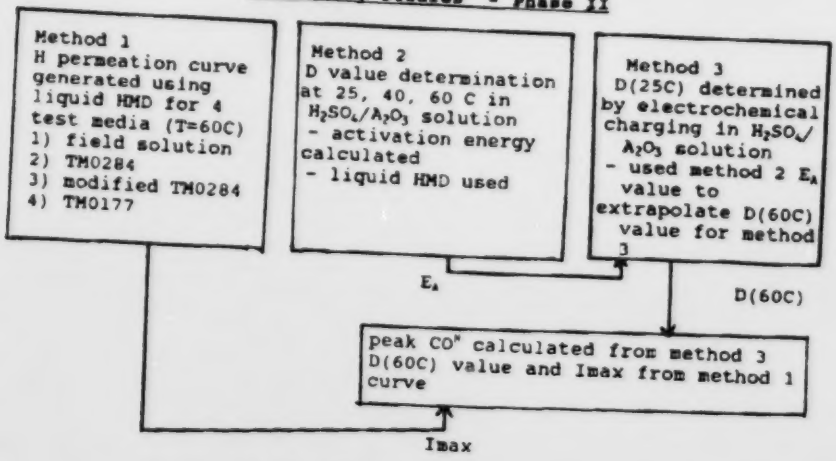
APPENDIX I A

Flow Chart of Methodology of Research Project

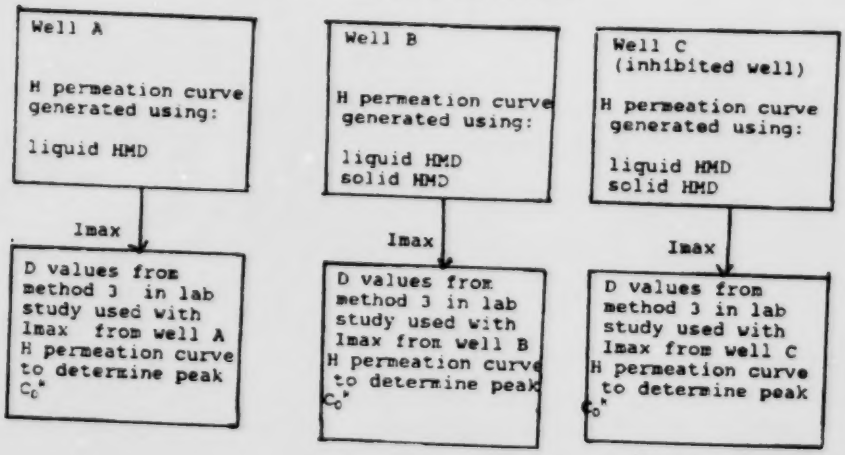
Lab Studies - Phase I



Laboratory Studies - Phase II


Method 1
H permeation curve generated using liquid HMD for 4 test media (T=60C)
1) field solution
2) TM0284
3) modified TM0284
4) TM0177
Method 2
D value determination at 25, 40, 60 C in H_2SO_4/A_2O_3 solution
- activation energy calculated
- liquid HMD used
Method 3
D(25C) determined by electrochemical charging in H_2SO_4/A_2O_3 solution
- used method 2 E_A value to extrapolate D(60C) value for method 3
E_A
D(60C)
peak CO* calculated from method 3 D(60C) value and Imax from method 1 curve
Imax

Field Studies - Phase III


Well A
H permeation curve generated using:
liquid HMD
Imax
D values from method 3 in lab study used with Imax from well A H permeation curve to determine peak C_o^*
Well B
H permeation curve generated using:
liquid HMD
solid HMD
Imax
D values from method 3 in lab study used with Imax from well B H permeation curve to determine peak C_o^*
Well C (inhibited well)
H permeation curve generated using:
liquid HMD
solid HMD
Imax
D values from method 3 in lab study used with Imax from well C H permeation curve to determine peak C_o^*

Appendix 1B. Hydrogen concentration in AM-2.

Temp ≈60°C	No inhibitor					
	Method 1†		Method 2*		Method 3**	
Solutions	D_{Avg} (6) (cm^2/s)	C_O^H (μ moles/cm^3)	$D_{H_2SO_4/As_2O_3}$ (cm^2/s)	C_O^H (μ moles/cm^3)	$D_{H_2SO_4/As_2O_3}$ (cm^2/s)	C_O^H (μ moles/cm^3)
Field water	0.147×10^{-6}	12	1.7×10^{-6}	1	4.8×10^{-6}	0.4
TM-02-84	0.313×10^{-6}	57	1.7×10^{-6}	10	4.8×10^{-6}	4
CSA	3.2×10^{-6}	114	1.7×10^{-6}	214	4.8×10^{-6}	76
TM-01-77	1.3×10^{-6}	177	1.7×10^{-6}	135	4.8×10^{-6}	48
	With inhibitor (not saturated with H_2S at t = 0)					
Field water	N.D.	N.D.	1.7×10^{-6}	N.D.	4.8×10^{-6}	N.D.
TM-02-84	0.69×10^{-6}	22.5	1.7×10^{-6}	9	4.8×10^{-6}	3
CSA	0.305×10^{-6}	44	1.7×10^{-6}	8	4.8×10^{-6}	3
TM-01-77	0.813×10^{-6}	125	1.7×10^{-6}	60	4.8×10^{-6}	21

† Solution not saturated with H_2S at t = 0.
* No electrochemical charging.
** Obtained by electrochemical charging.

Field results - liquid HMD.

Temp ≈60°C	No inhibitor					
	Method 1		Method 2*		Method 3**	
Field water	D_{Avg} (6) (cm^2/s)	C_O^H (μ moles/cm^3)	$D_{H_2SO_4/As_2O_3}$ (cm^2/s)	C_O^H (μ moles/cm^3)	$D_{H_2SO_4/As_2O_3}$ (cm^2/s)	C_O^H (μ moles/cm^3)
Well A 9.5% H_2S	0.9×10^{-6}	49	1.7×10^{-6}	26	4.8×10^{-6}	9
Well B 15.8% H_2S	2.5×10^{-6}	88	1.7×10^{-6}	129	4.8×10^{-6}	32-46
Well C 17.6% H_2S	–	94***				49***
	With inhibitor					
Well C 17.6% H_2S	1.1×10^{-6}	12	1.7×10^{-6}	7	4.8×10^{-6}	3

* No electrochemical charging.
** Obtained by electrochemical charging.
*** Extrapolated value based on per cent H_2S..

APPENDIX 2

EVALUATION OF THE PERMEATION CURVE

A schematic of a hydrogen permeation vs time curve for steel in a sour environment is given in Fig. 6. The permeation curve characteristically shows a maximum that is not expected on the basis of nonsteady-state diffusion theory. The maximum is commonly attributed to the formation of an FeS layer, blistering of the steel surface, or disturbances in the sour medium/steel interface equilibria (10,11), whereas the influence of surface oxides has also been mentioned (12). Thus far, the origin of the maximum has not been unequivocally established. Since the above effects are time dependent, we may expect the theoretical transients to apply only at the beginning of the permeation, i.e., when the influence of the above factors is still negligible.

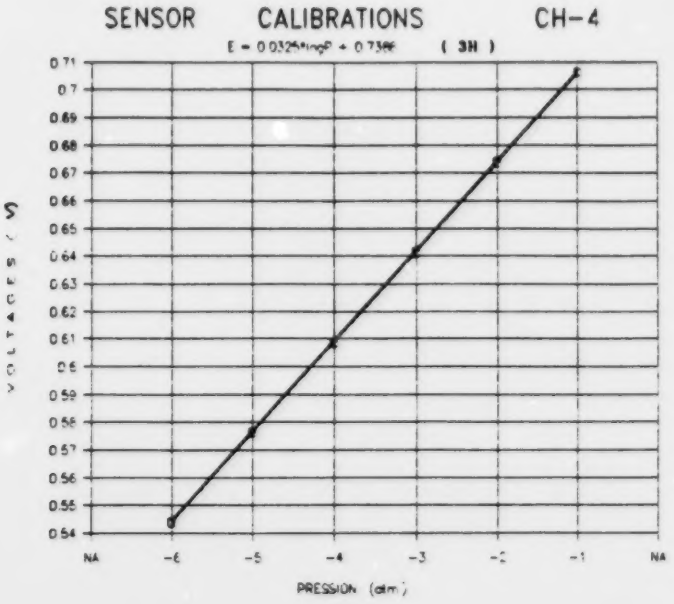
The method used to calculate D was based on the permeation current transient at short exposure times (13):

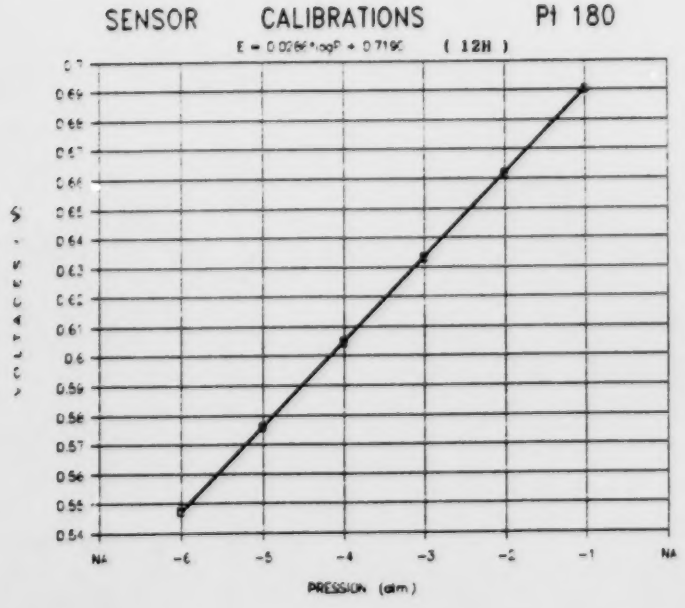
$$\frac{I(t_1)}{I(t_2)} = \sqrt{\frac{t_2}{t_1}} \times e^{-\frac{L^2}{4D}\left(\frac{1}{t_1}-\frac{1}{t_2}\right)}$$

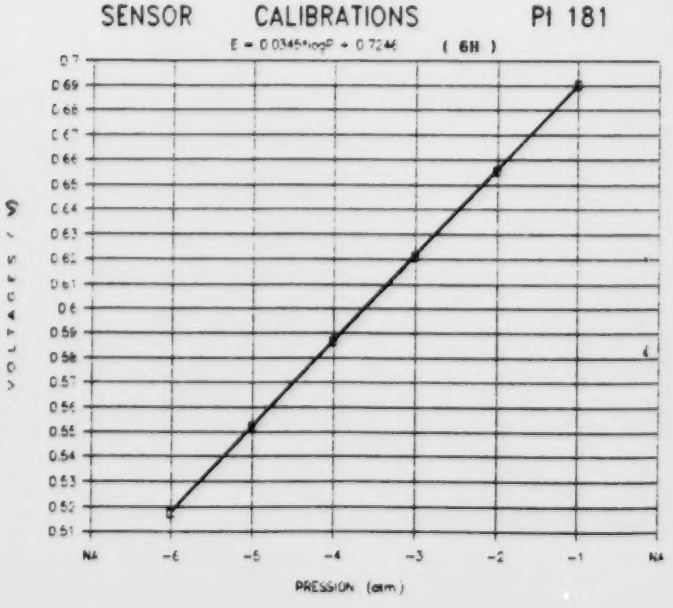
where $I(t_1)$ and $I(t_2)$ are the current densities at times t_1 and t_2, respectively, measured from t_0 (time = 0). The six values of D are averaged from four pairs of values I_{nt} and t_n (I_{t1} = 5% I_{max}, I_{t2} = 10% I_{max}, I_{t3} = 15% I_{max} and I_{t4} = 20% I_{max}).

APPENDIX 3

CALIBRATION DATA FOR THE SOLID-STATE HMD





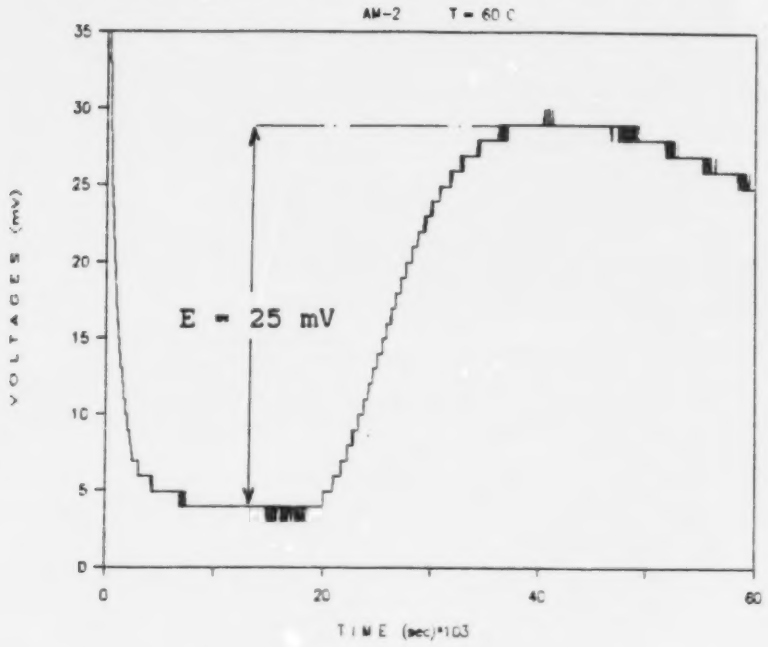


APPENDIX 4

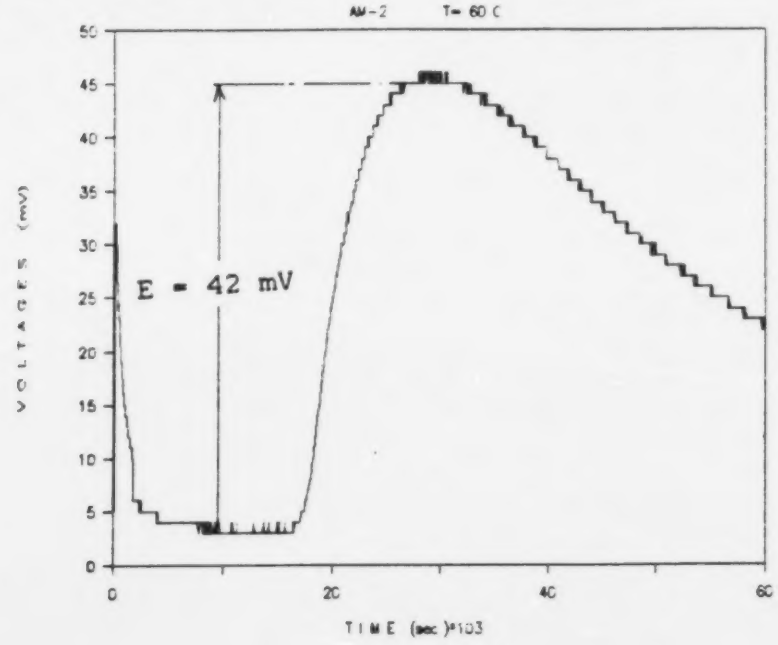
EXPERIMENTAL HYDROGEN PERMEATION CURVES OBTAINED IN THE LABORATORY AND FIELD EXPERIMENTS

LIQUID HMD

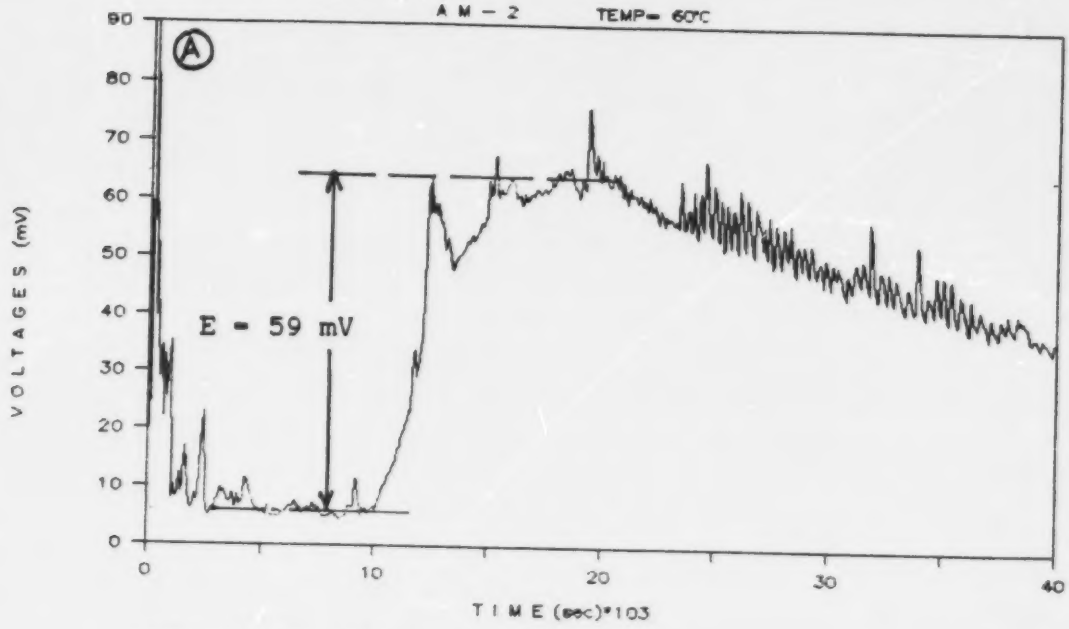
FIELD PRODUCED SOLUTION (Presaturated with H_2S)



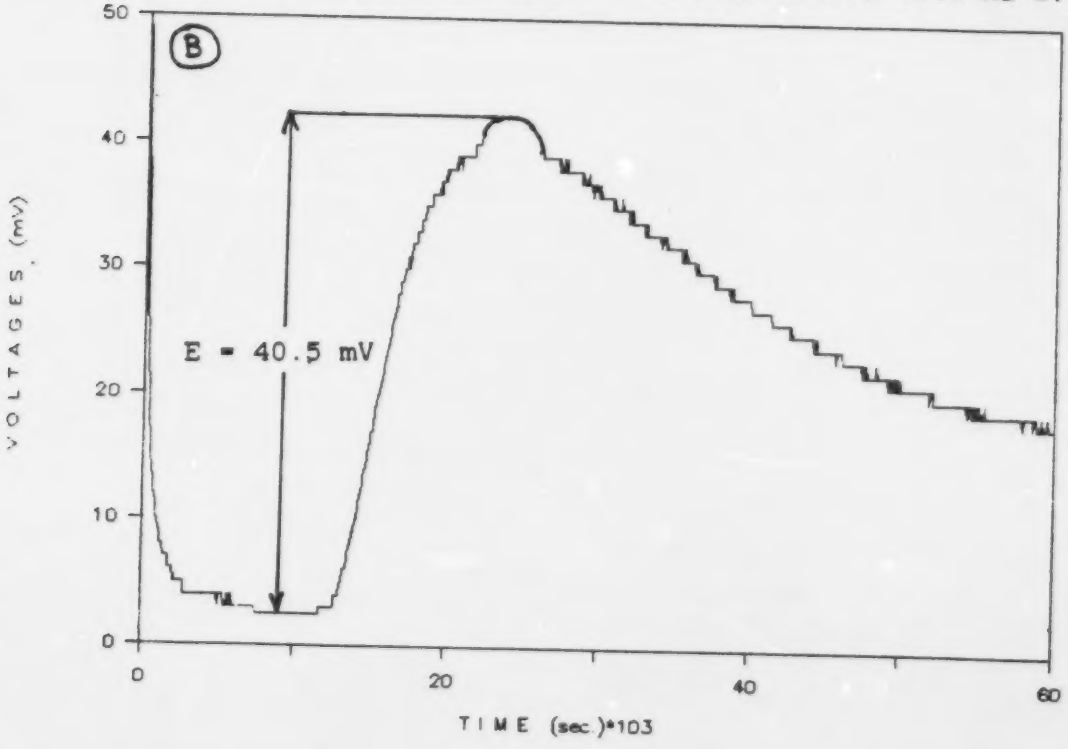
LIQUID HMD TM-02-84 (Presaturated with H_2S)



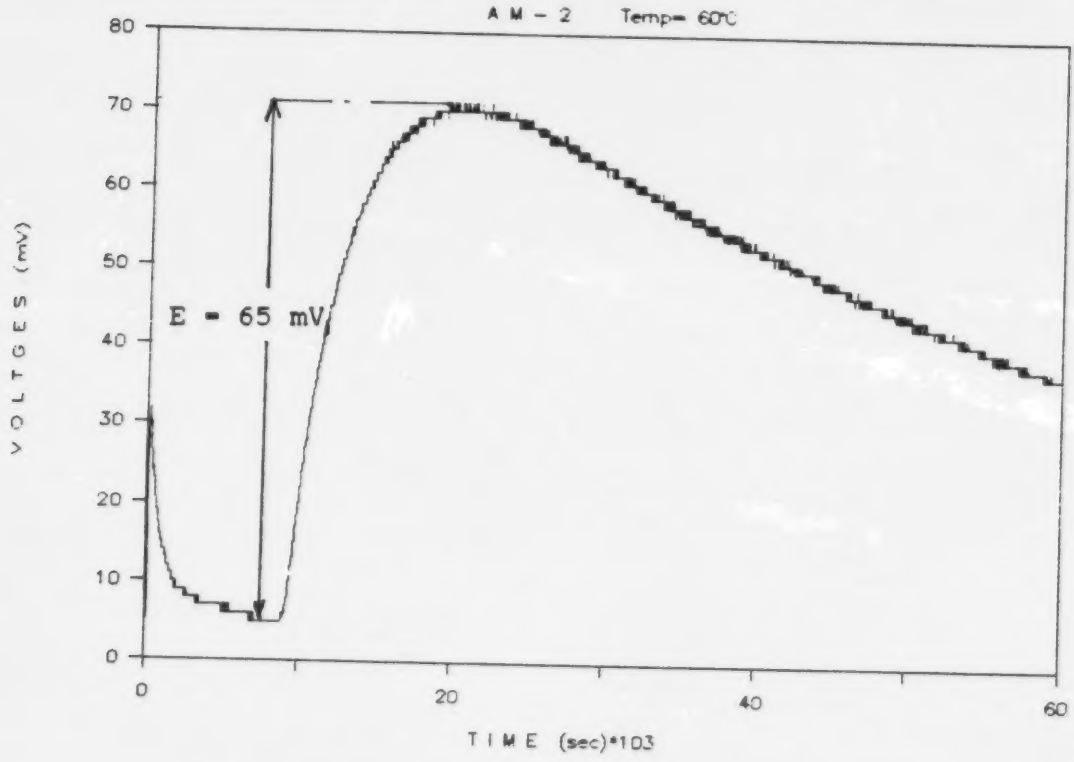
LIQUID HMD MODIFIED TM-02-84 (Presaturated with H_2S)



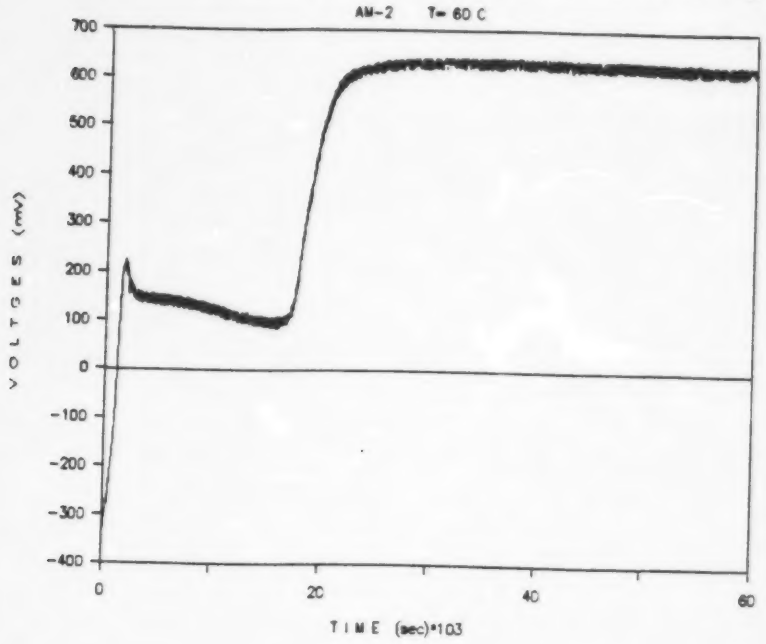
LIQUID HMD MODIFIED TM-02-84 (Presaturated with H_2S)



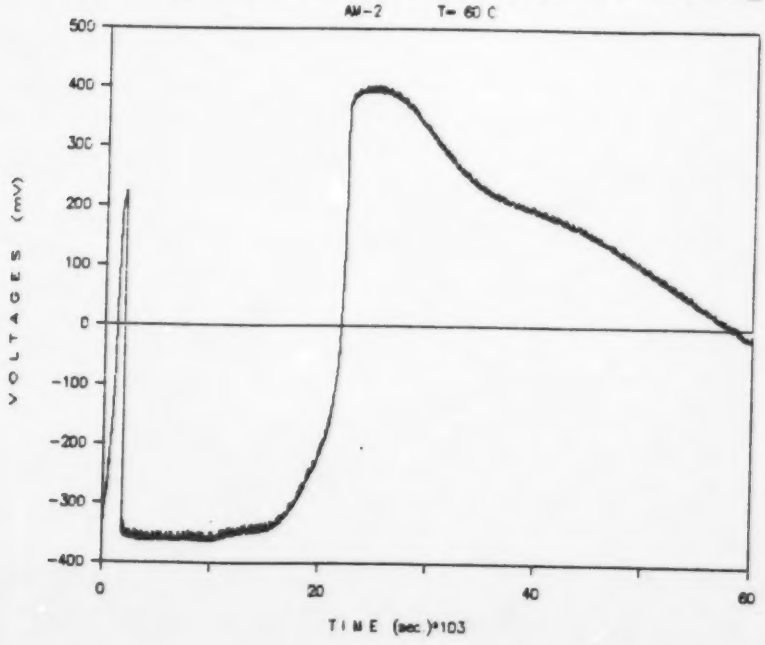
LIQUID HMD TM-01-77 (Presaturated with H_2S)

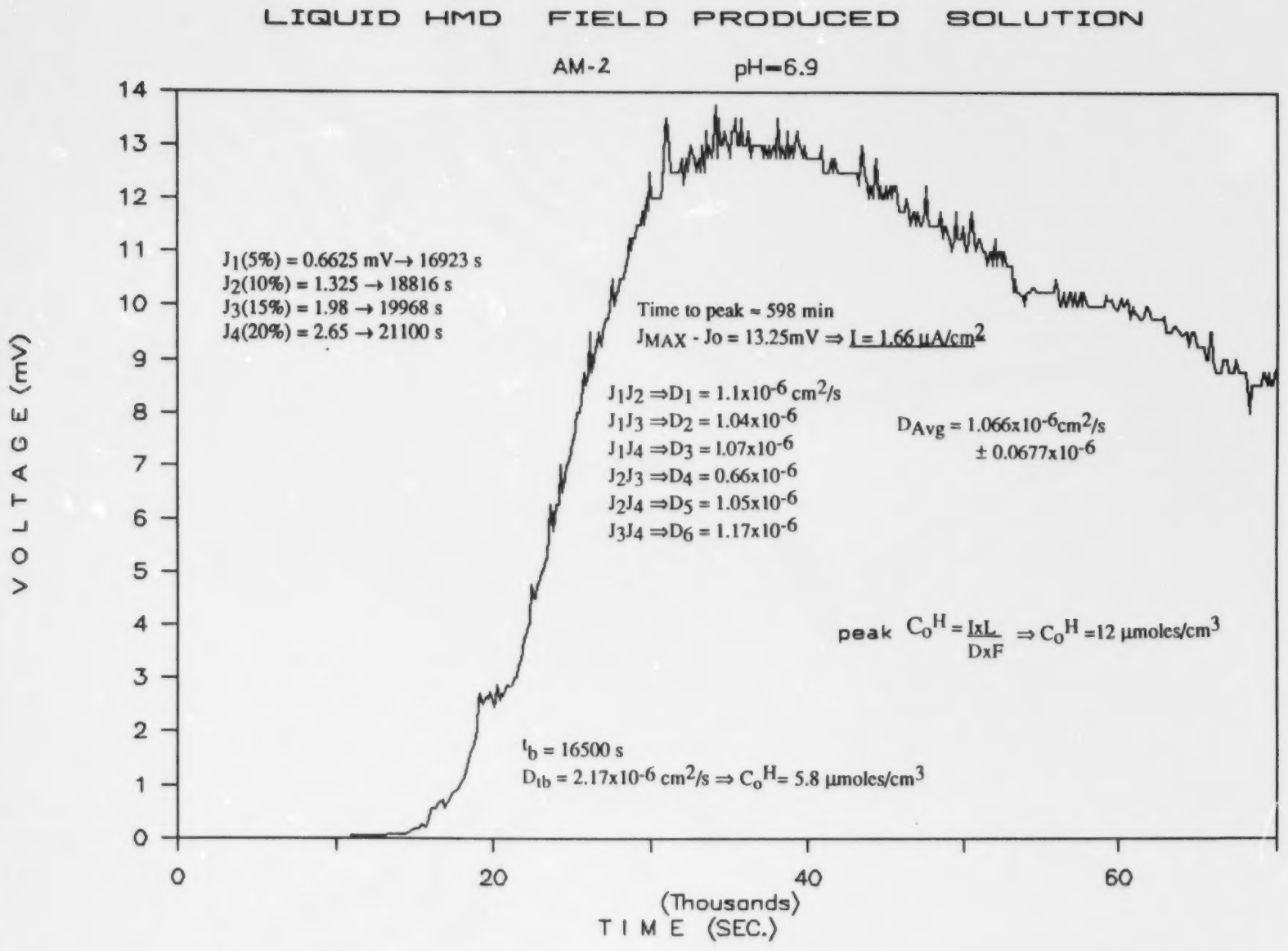


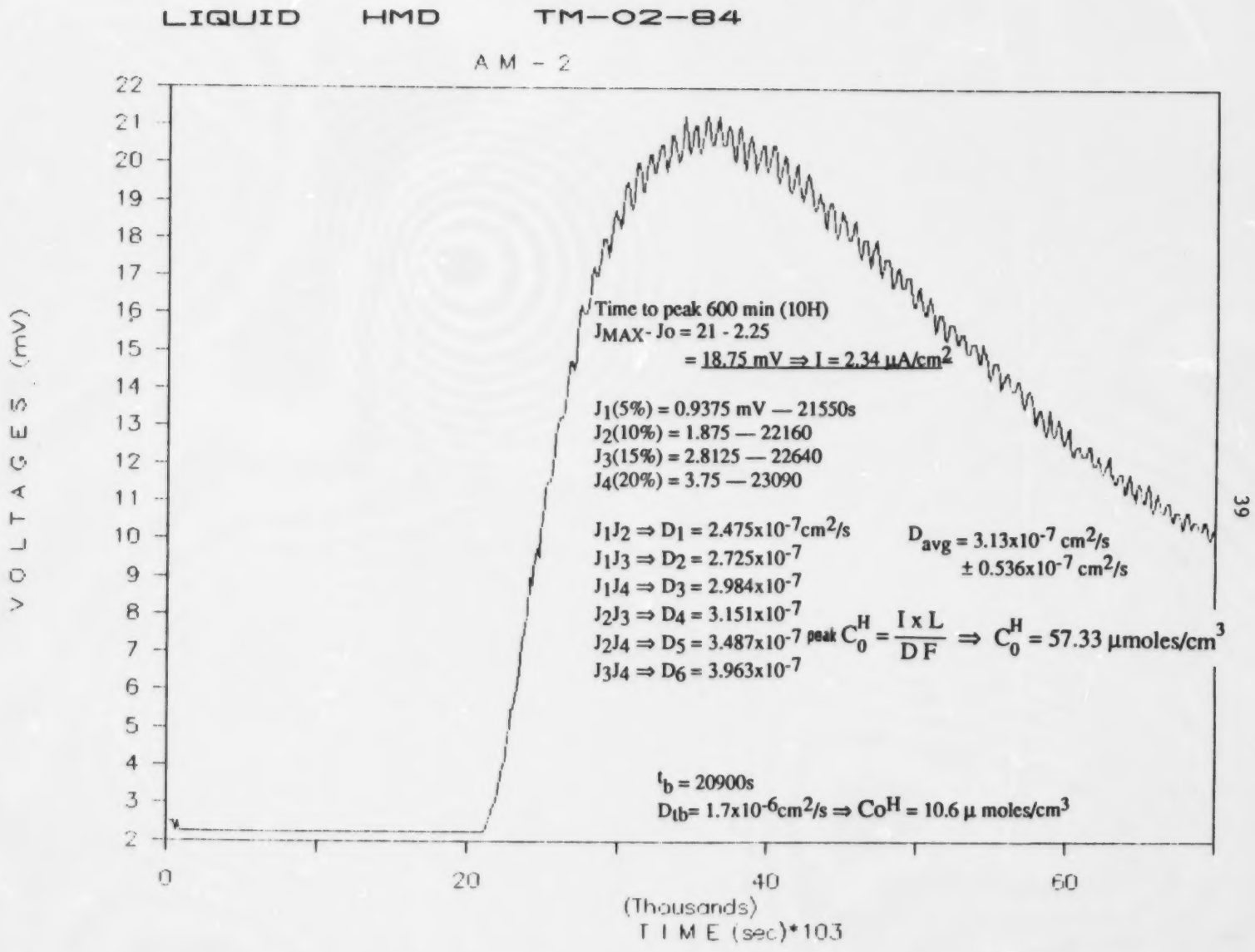
SOLID HMD TM-01-77 (Presaturated with H_2S)

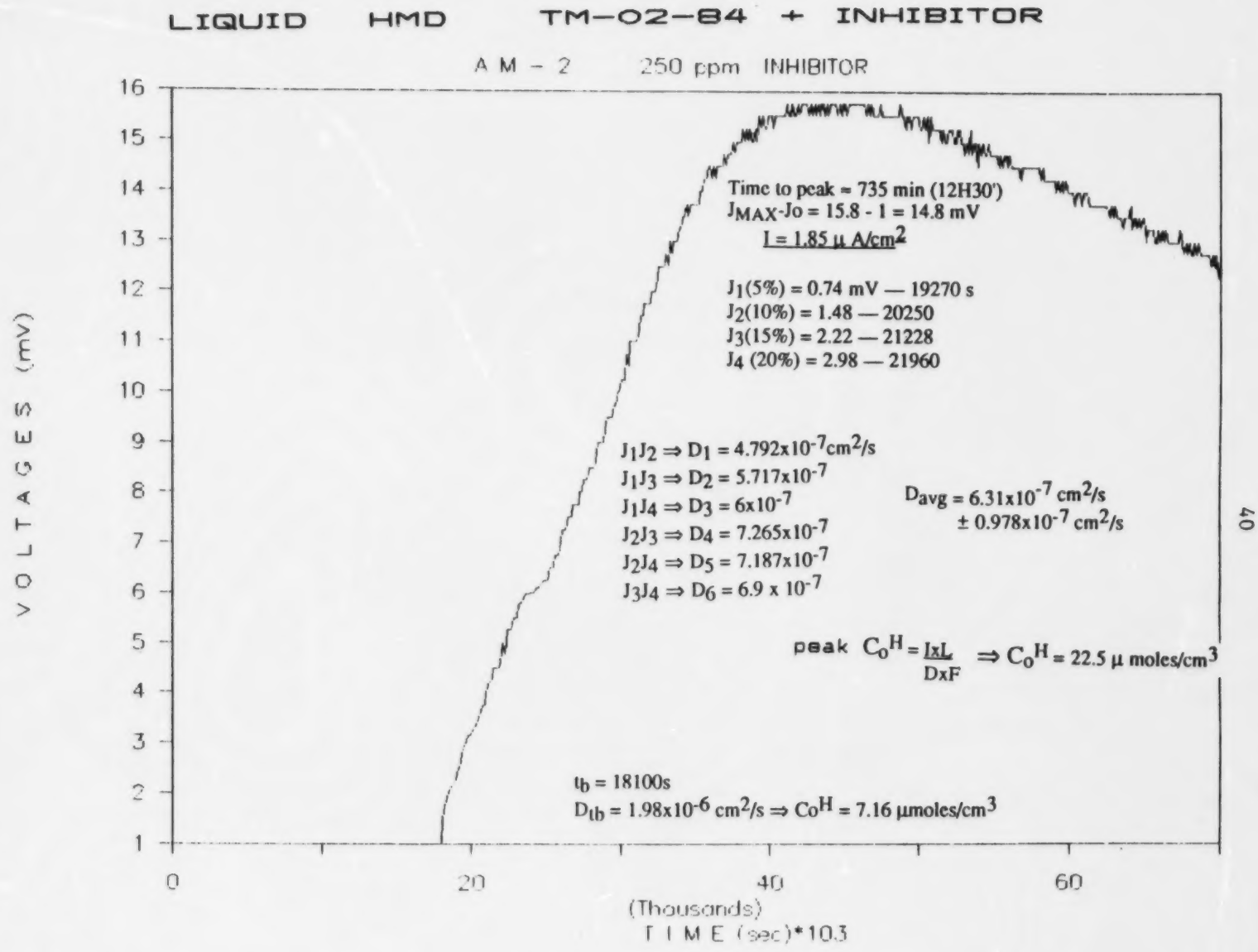


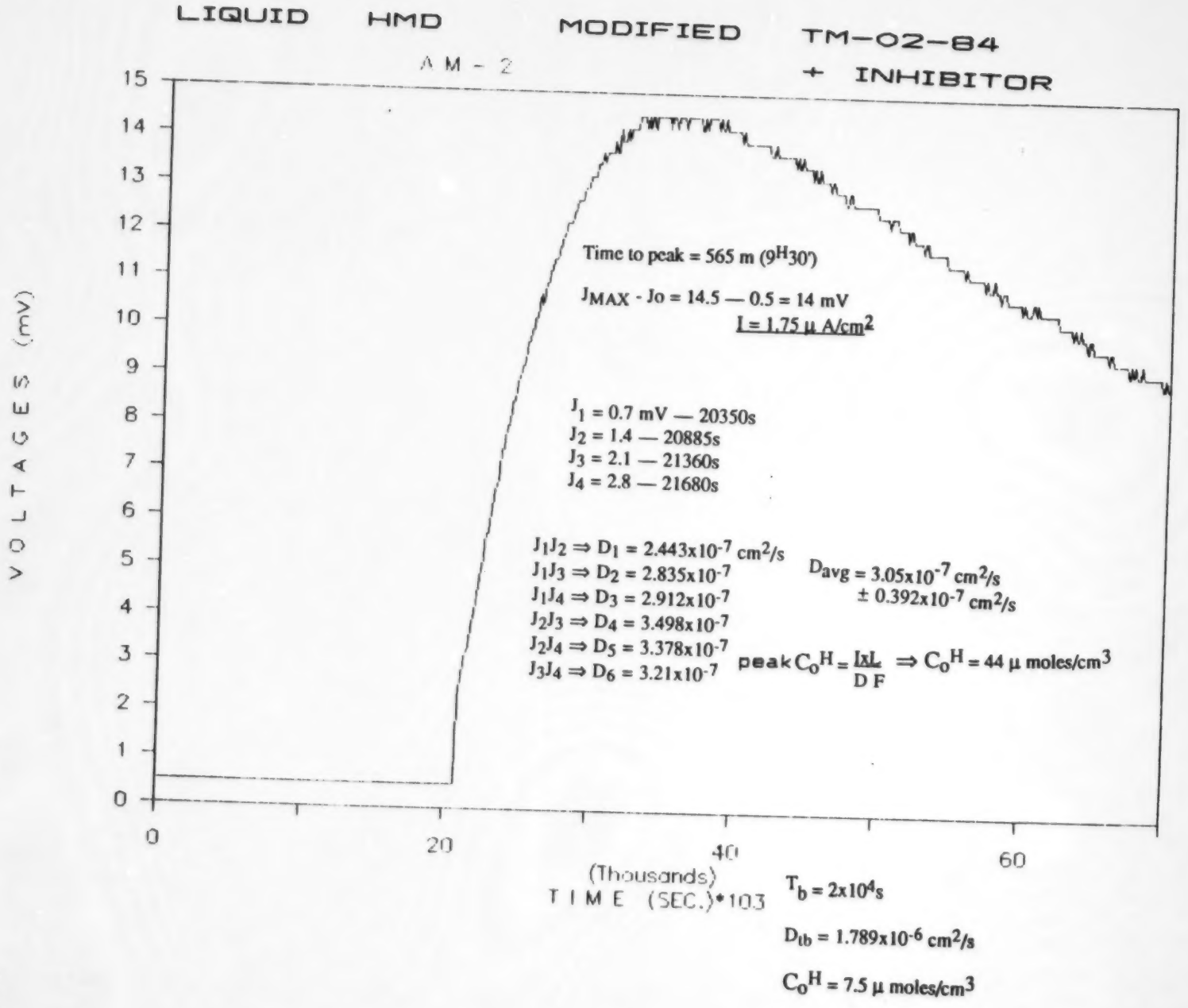
SOLID HMD TM-02-84 (Presaturated with H_2S)

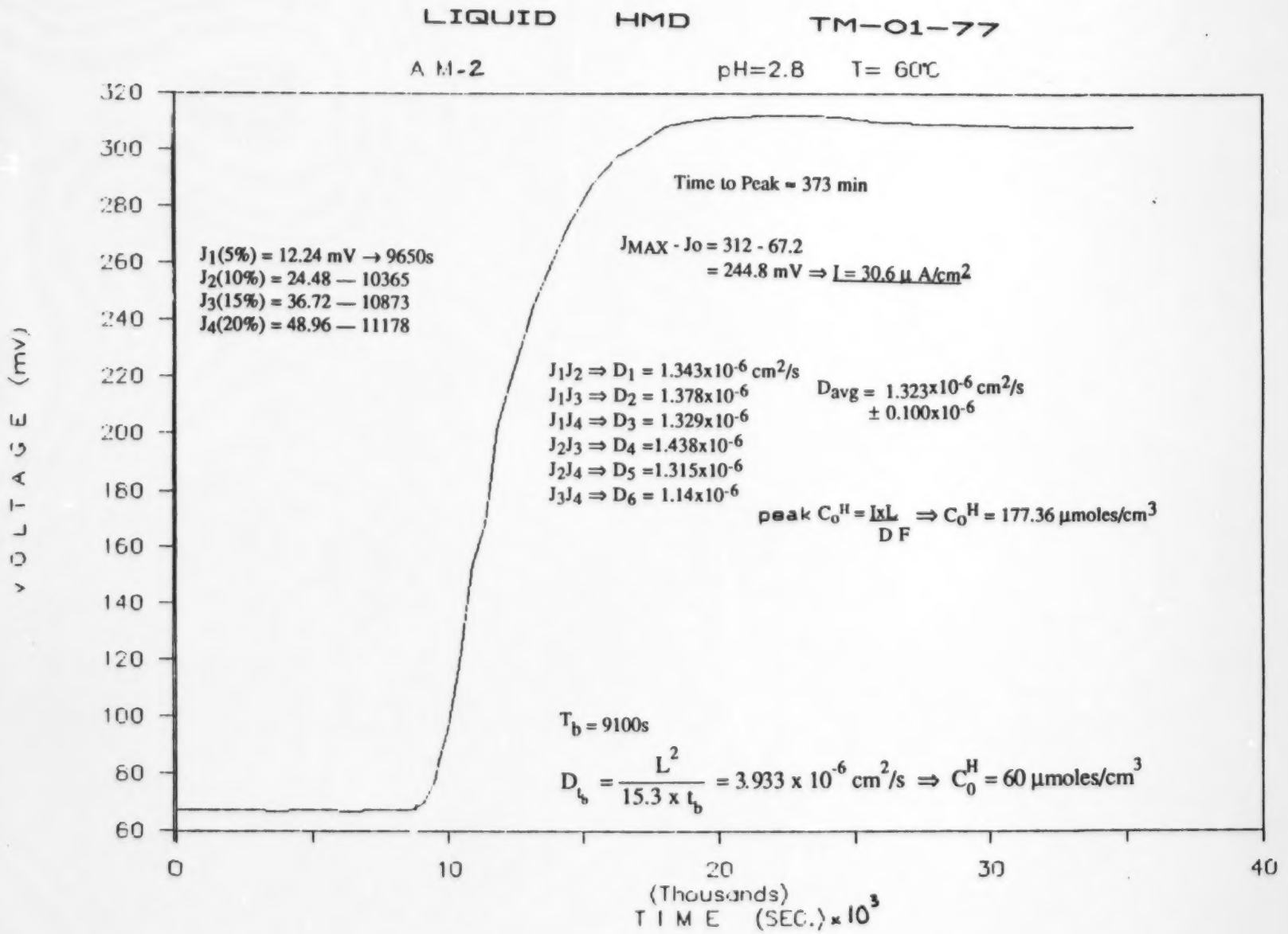


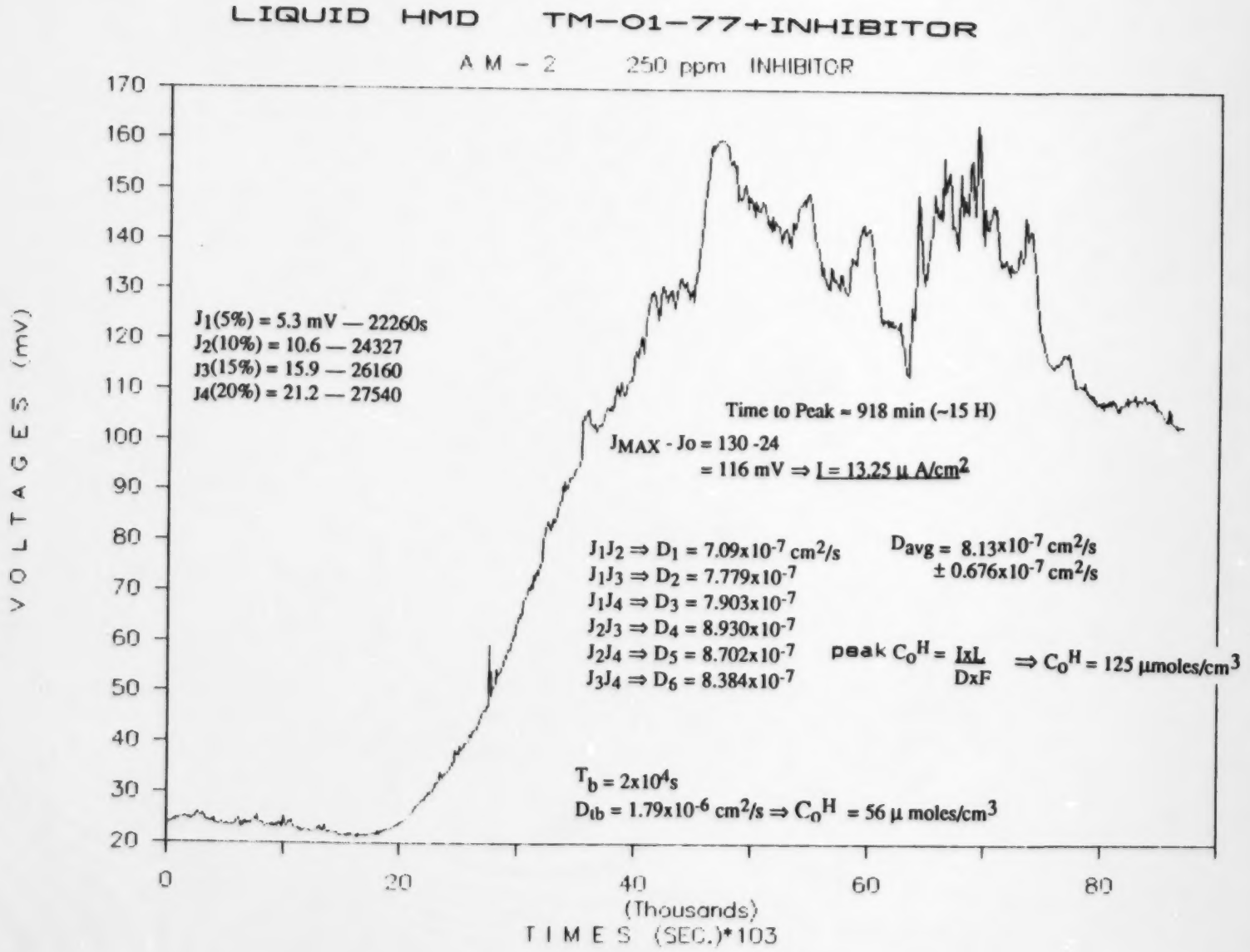

LIQUID HMD FIELD PRODUCED SOLUTION
AM-2 pH=6.9
VOLTAGE (mV)
TIME (SEC.)
(Thousands)
0
20
40
60
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
J1(5%) = 0.6625 mV→ 16923 s
J2(10%) = 1.325 → 18816 s
J3(15%) = 1.98 → 19968 s
J4(20%) = 2.65 → 21100 s
Time to peak ≈ 598 min
JMAX - Jo = 13.25mV ⇒ I = 1.66 μA/cm2
J1J2 ⇒D1 = 1.1x10-6 cm2/s
J1J3 ⇒D2 = 1.04x10-6
J1J4 ⇒D3 = 1.07x10-6
J2J3 ⇒D4 = 0.66x10-6
J2J4 ⇒D5 = 1.05x10-6
J3J4 ⇒D6 = 1.17x10-6
DAvg = 1.066x10-6cm2/s
± 0.0677x10-6
peak CoH = IxL / DxF ⇒ CoH =12 μmoles/cm3
tb = 16500 s
Dtb = 2.17x10-6 cm2/s ⇒ CoH= 5.8 μmoles/cm3


LIQUID HMD TM-02-84
A M - 2
VOLTAGES (mV)
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
0
20
40
60
(Thousands)
T I M E (sec)*103
Time to peak 600 min (10H)
JMAX - Jo = 21 - 2.25
= 18.75 mV ⇒ I = 2.34 μA/cm2
J1(5%) = 0.9375 mV — 21550s
J2(10%) = 1.875 — 22160
J3(15%) = 2.8125 — 22640
J4(20%) = 3.75 — 23090
J1J2 ⇒ D1 = 2.475x10-7cm2/s
J1J3 ⇒ D2 = 2.725x10-7
J1J4 ⇒ D3 = 2.984x10-7
J2J3 ⇒ D4 = 3.151x10-7
J2J4 ⇒ D5 = 3.487x10-7
J3J4 ⇒ D6 = 3.963x10-7
Davg = 3.13x10-7 cm2/s
± 0.536x10-7 cm2/s
peak C0H = I x L / D F ⇒ C0H = 57.33 μmoles/cm3
tb = 20900s
Dtb= 1.7x10-6cm2/s ⇒ CoH = 10.6 μ moles/cm3


LIQUID HMD TM-02-84 + INHIBITOR
A M - 2 250 ppm INHIBITOR
VOLTAGES (mV)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
20
40
60
(Thousands)
T I M E (sec)*10.3
Time to peak = 735 min (12H30')
J_{MAX}-Jo = 15.8 - 1 = 14.8 mV
I = 1.85 μ A/cm^2
J_1(5%) = 0.74 mV — 19270 s
J_2(10%) = 1.48 — 20250
J_3(15%) = 2.22 — 21228
J_4 (20%) = 2.98 — 21960
$J_1J_2 \Rightarrow D_1 = 4.792 \times 10^{-7} cm^2/s$
$J_1J_3 \Rightarrow D_2 = 5.717 \times 10^{-7}$
$J_1J_4 \Rightarrow D_3 = 6 \times 10^{-7}$
$J_2J_3 \Rightarrow D_4 = 7.265 \times 10^{-7}$
$J_2J_4 \Rightarrow D_5 = 7.187 \times 10^{-7}$
$J_3J_4 \Rightarrow D_6 = 6.9 \times 10^{-7}$
$D_{avg} = 6.31 \times 10^{-7} cm^2/s$
$\pm 0.978 \times 10^{-7} cm^2/s$
peak $C_o^H = \frac{IxL}{DxF} \Rightarrow C_o^H = 22.5 \mu moles/cm^3$
$t_b = 18100s$
$D_{tb} = 1.98 \times 10^{-6} cm^2/s \Rightarrow Co^H = 7.16 \mu moles/cm^3$


LIQUID HMD MODIFIED TM-02-84
+ INHIBITOR
AM - 2
VOLTAGES (mV)
TIME (SEC.)*103
(Thousands)
Time to peak = 565 m (9H30')
JMAX - Jo = 14.5 — 0.5 = 14 mV
I = 1.75 μ A/cm2
J1 = 0.7 mV — 20350s
J2 = 1.4 — 20885s
J3 = 2.1 — 21360s
J4 = 2.8 — 21680s
J1J2 ⇒ D1 = 2.443x10-7 cm2/s
J1J3 ⇒ D2 = 2.835x10-7
J1J4 ⇒ D3 = 2.912x10-7
J2J3 ⇒ D4 = 3.498x10-7
J2J4 ⇒ D5 = 3.378x10-7
J3J4 ⇒ D6 = 3.21x10-7
Davg = 3.05x10-7 cm2/s
± 0.392x10-7 cm2/s
peak CoH = IxL / DF ⇒ CoH = 44 μ moles/cm3
Tb = 2x10^4s
Dtb = 1.789x10-6 cm2/s
CoH = 7.5 μ moles/cm3


LIQUID HMD TM-01-77
A M-2
pH=2.8 T= 60°C
VOLTAGE (mV)
320
300
280
260
240
220
200
180
160
140
120
100
80
60
0
10
20
30
40
(Thousands)
TIME (SEC.) x 10^3
Time to Peak = 373 min
J1(5%) = 12.24 mV → 9650s
J2(10%) = 24.48 — 10365
J3(15%) = 36.72 — 10873
J4(20%) = 48.96 — 11178
JMAX - Jo = 312 - 67.2
= 244.8 mV ⇒ I = 30.6 μ A/cm2
J1J2 ⇒ D1 = 1.343x10-6 cm2/s
J1J3 ⇒ D2 = 1.378x10-6
J1J4 ⇒ D3 = 1.329x10-6
J2J3 ⇒ D4 =1.438x10-6
J2J4 ⇒ D5 =1.315x10-6
J3J4 ⇒ D6 = 1.14x10-6
Davg = 1.323x10-6 cm2/s
± 0.100x10-6
peak Co^H = IxL / DF ⇒ Co^H = 177.36 μmoles/cm3
Tb = 9100s
Dtb = L^2 / 15.3 x tb = 3.933 x 10-6 cm2/s ⇒ C0^H = 60 μmoles/cm3


LIQUID HMD TM-01-77+INHIBITOR
A M - 2 250 ppm INHIBITOR
VOLTAGES (mV)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
0
20
40
60
80
(Thousands)
TIMES (SEC.)*103
J1(5%) = 5.3 mV — 22260s
J2(10%) = 10.6 — 24327
J3(15%) = 15.9 — 26160
J4(20%) = 21.2 — 27540
Time to Peak = 918 min (~15 H)
JMAX - Jo = 130 -24
= 116 mV ⇒ I = 13.25 μ A/cm2
J1J2 ⇒ D1 = 7.09x10-7 cm2/s
J1J3 ⇒ D2 = 7.779x10-7
J1J4 ⇒ D3 = 7.903x10-7
J2J3 ⇒ D4 = 8.930x10-7
J2J4 ⇒ D5 = 8.702x10-7
J3J4 ⇒ D6 = 8.384x10-7
Davg = 8.13x10-7 cm2/s
± 0.676x10-7 cm2/s
peak CoH = IxL / DxF ⇒ CoH = 125 μmoles/cm3
Tb = 2x10^4s
Dtb = 1.79x10-6 cm2/s ⇒ CoH = 56 μ moles/cm3